

COUNTERCURRENT DISTRIBUTION OF HIGH-BOILING NEUTRAL OILS FROM A LOW-TEMPERATURE COAL TAR

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INTRODUCTION

In a comprehensive investigation of the composition of low-temperature bituminous coal tar it was necessary to analyze the high-boiling neutral oil fractions in the range 275° to 344° C. The method selected for this was fractionation by distillation, further separation by countercurrent distribution (CCD), and final analysis by infrared and ultraviolet spectrophotometry. A recent review on countercurrent distribution (10) shows that relatively little work has been done on the CCD of high-boiling neutral polynuclear compounds and nothing on separation of natural mixtures by this method. Golumbic (8) has reported an investigation of the partition coefficient of 18 polynuclear compounds in the solvent system cyclohexane/80 percent ethanol and proposed this solvent system for the analysis of the heavy-oil fractions of coal-hydrogenation products. Chang (5) reported on the partition coefficient of 24 aromatic compounds in β, β' -oxydipropionitrile/isooctane and proposed this solvent system for CCD separations of petroleum fractions and oils derived from coal tars. Mold (11) has recently conducted work on the CCD of polycyclic aromatic compounds with a solvent system containing tetramethyluric acid but did not analyze natural mixtures. The present work fully demonstrates the capabilities of CCD, supplemented by infrared and ultraviolet spectroscopy for the separation and analysis of complex high-boiling neutral aromatic coal tar, shale oil, or petroleum components. It was found that class separations were sufficient to allow reliable spectrophotometric analyses to be applied. Many specific isomers occurring in sufficiently large enough amounts were individually determined.

EXPERIMENTAL

Preliminary Fractionation by Distillation. - The neutral oil used in this work was obtained from a low-temperature West Virginia bituminous coal tar. Previous reports (3, 4) have presented the analysis of this material for fractions up to the present boiling range, using gas-liquid chromatography. In two separate distillations, the 29 neutral oil fractions analyzed in the present work were obtained, these representing 33.46 wt pct of the total neutral oil (the total neutral oil distilling up to about 360° C represents 16.92 wt pct of the tar). Complete data for the first of these distillations, including analysis of fractions 1 to 8, is included in a previous paper (3). The second distillation was made on a 47.2 g charge, giving 38.7 g distillate, 7.7 g residue, and 0.9 g loss and hold up. This material was distilled at 3.0 mm Hg with a reflux ratio of 20 to 1 in a spinning band still. Equivalent atmospheric boiling points were estimated from a standard nomograph. Infrared and ultraviolet spectra were obtained on all distillate fractions. These were combined on the basis of qualitative similarity to give 14 samples which were each fractionated by countercurrent distribution.

Countercurrent Distribution. - The instrument used was a Craig 60-tube all-glass model with an automatic fraction collector. The tube capacity for each phase was 40 ml. The instrument was operated to give 120 transfers and 60 tubes were collected in the fraction collector. Each distribution was made with a charge of 500 milligrams, obtained by using the proper volume of a solution of known concentration of the distillate fraction in the upper phase. The upper phase solvent was spectral grade isooctane, and the lower phase was a 90 wt pct ethanol in water mixture. This solvent system was chosen on the basis of its ability to separate various aromatic hydrocarbons from each other. A thorough investigation was conducted on anthracene, a typical component of these neutral oil fractions. Its partition coefficient in a variety of solvent pairs was determined, and the final choice was made for that in which the value was nearest 1. This placed the bulk of the material where enough tubes could be efficiently utilized in the separations. The solvent system choice was also limited to those mixtures sufficiently immiscible to give complete separation of layers during the preset instrument cycling time. The distributions were carried out at 26° C, and the solvents were pre-equilibrated at the same temperature. This pre-equilibration produced a volume change for equal volumes to 1.83 parts 90 wt pct ethanol per 1.00 parts isooctane after equilibration. The equilibrated solvents were used in making all necessary dilutions for ultraviolet analysis.

Spectrophotometric Analysis. - Ultraviolet spectra were obtained on the contents of all CCD tubes, taken directly from the instrument, on a Perkin-Elmer Model 350 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer equipped with a Perkin-Elmer 6x ultramicro sampling unit mounted in the sample beam. The sample holder, designed to mount the ultramicrocavity cells in this unit, has been described (6). Sample preparation preceding infrared analysis was as follows:

The contents of a single tube after ultraviolet analysis were placed in a 150-ml distillation flask and dry nitrogen passed slowly into the flask through a glass tube extending nearly to the bottom of the flask where the tube was drawn into a fine tip. The nitrogen flowed out through the side arm. When the solvent was completely removed, the material was transferred from this flask by means of a 6-in. hypodermic needle and syringe and several washings of carbon disulfide into a small tared tapered tube. The CS₂ was evaporated from this small tube with nitrogen through a syringe needle. It was seen from infrared spectra that the last traces of CS₂ could be removed by this method. The small amount of liquid material in the tip of this tube was first weighed and then transferred with the aid of a 50 μl microsyringe to an ultramicrocavity NaCl cell (purchased from the Barnes Engineering Company). Samples were run undiluted in these cells whenever possible. When there was not enough sample recovered to fill the cell cavity, the material was diluted with CS₂ and the infrared spectrum obtained in solution.

Determination of Distribution Curves. - The amount of material recovered in each tube was plotted to obtain a weight distribution for each run. The amount of material in a single tube typically ranged from 0.5 to 21 milligrams. Ultraviolet absorbance distribution curves also were prepared at various key wavelengths for each run. These were used for the determination of peak tubes of major components and in the quantitative analysis. When there was no peak tube discernible on the distribution plot for minor or trace components determined to

be present from spectra, it was possible to resolve the "envelope" of ultraviolet absorbance into its component parts. Since the countercurrent distributions are essentially Gaussian and symmetrical, it is possible to construct individual absorbance distribution curves by following the appearance and disappearance of individual bands in consecutive fractions and noting the peak tubes from spectra. This procedure was also helpful in determining which bands belonged to the same compound.

RESULTS AND DISCUSSION

The results of the distillations are given in Table 1. On the basis of the qualitative information from ultraviolet and infrared spectra, the constituents from each CCD fractionation were distinguished and assigned numbers. It was essential to number these constituents since they frequently appeared in more than one run. A total of 51 separate identifications were made in this 69° C boiling range, and these are shown in Table 2.

The quantitative analyses for aromatics were conducted in the ultraviolet using absorptivities at characteristic bands where interferences from other constituents were at a minimum. Absorbance values were obtained from the curves already described. Where the ultraviolet absorption bands for components overlapped too greatly, their relative amounts could generally be estimated from their infrared bands. In those instances where very similar isomers overlapped extensively, they were analyzed as a class rather than as individual compounds. The qualitative and quantitative analyses of each class are described under separate headings.

From the quantitative data obtained for each constituent, plots of milligrams vs. tube number were prepared. Figures 1, 2, and 3 show these distribution curves for only 3 of the 14 neutral oil fractions. These are for CCD numbers 4, 9, and 14. Tubes are numbered from 0 to 59 in the direction of transfer in the instrument and from 0 up in the order of use in the fraction collector. The numbers on the distribution curves in Figures 1, 2, and 3 refer to some of the constituents listed in Table 2. The weight-percent of each constituent in the neutral oil was obtained from the distribution curves and the weights of the original distillate fractions. These quantitative results are summarized in Table 3.

o-Dimethylphthalate. - Identification of this compound was made by infrared spectroscopy. Its location in the lower tube numbers of the lower phase is in line with its polarity.

Carbazoles. - The weak but significant polar character of the unsubstituted nitrogen atom of carbazoles places this class in the lower numbered tubes of the lower phase, beginning with the parent structure in tube 27 of CCD No. 9. Subsequent runs show the peak tube to shift to tubes 29 and 31, indicating methylation, and both infrared and ultraviolet spectra confirmed the presence of monomethyl carbazoles. The quantitative determination of carbazole and its methyl derivatives was straightforward, using the absorption band at 230 to 240 μ . For the determination of the mixed monomethyl isomers, the absorptivity data used was obtained from available samples of 1- and 2-methylcarbazole. Infrared literature spectra were available for the 3- and 4-methylcarbazoles (12), and ultraviolet was available for 3-methylcarbazole (9).

Long-chain Aliphatic Hydrocarbons. - These were effectively separated from aromatic hydrocarbons in the first 15 tubes of the fraction collector in each CCD run. Infrared analysis (7) showed this aliphatic material to consist of five classes: α -olefins, branched α -olefins, trans-internal olefins, n-alkanes, and 2-methylalkanes. Since the CCD solvent system was selected for optimum separation of aromatics, there was only a small separation by class for the aliphatic compounds. In Table 2 each class was assigned a single number throughout the entire boiling range although boiling points indicate a change in molecular weight from C_{15} through C_{20} .

Alkyl naphthenes. - According to Bellamy (2), the infrared bands observed at 10.72, 10.50, 10.27, and 9.73 μ in aliphatic fractions can be assigned to the ring deformation vibrations of six-membered ring naphthenes. An estimate of their concentration was made using data from literature spectra (1).

Aliphatic Carbonyl. - The carbonyl bands at 5.72 to 5.93 μ along with the CH_2 rocking vibration at 13.88 μ were assigned to aliphatic carbonyl, either ketones or esters. The fairly long chain, as indicated by the intensity of the 13.88 μ band, balances the polar effect of the carbonyl group to place them in tubes 56 to 58 of the fraction collector. Estimates of concentration for this class were made by using absorptivity data for the carbonyl band from pure samples of aliphatic esters.

Naphthalenes. - Alkyl naphthalenes were identified in all neutral oil fractions. On the basis of boiling point and ultraviolet correlations, it was found that they were predominantly polymethylnaphthalenes. There was no evidence of any long chain or branched alkyl substitution. Infrared bands at 6.25 and 9.67 μ along with strong out-of-plane hydrogen deformation vibration bands in the 11.0 to 14.0 μ region were observed. The increasing number of possible isomers with increasing molecular weight of methylnaphthalenes made identification of specific isomers extremely difficult. It was observed from this laboratory's data and a collection of methylnaphthalene spectra from the literature, that in general, for polymethylnaphthalenes the specific absorptivity of the 230 $m\mu$ band decreases regularly in intensity with increasing molecular weight. The values for each carbon number were in a range narrow enough to justify the use of an average. The average specific absorptivity for 14 trimethylnaphthalenes (C_{13}) was 530, for 7 tetramethylnaphthalenes (C_{14}), 442, for 3 pentamethylnaphthalenes (C_{15}), 346, and for 4 hexamethylnaphthalenes (C_{16}), 317. An average specific absorptivity of 7 literature ethylmethylnaphthalenes (C_{13}) falls very close to the value of trimethylnaphthalenes (C_{13}), and an average of 4 diethylmethylnaphthalenes (C_{15}) falls very close to that of pentamethylnaphthalenes (C_{15}).

Hydroaromatics and Biphenyls. - A broad ultraviolet band at 259 $m\mu$ at a maximum in tubes 11 to 14 FC represented a mixture of biphenyls and hydroaromatics. Biphenyls were indicated by a series of shoulders occurring on this major band and also by an infrared band at 14.30 μ . The hydroaromatic structure was indicated by the aromatic band at 6.25 μ which, although present, was relatively weak. Additional evidence to support this class was obtained from ultraviolet quantitative data. From the actual weight of these fractions and the observed absorbances, ultraviolet absorptivities were approximated and found to be low, indicating saturation of aromatic rings.

Fluorenes. - Fluorenes were identified by their distinctly characteristic ultraviolet spectra and their strong out-of-plane hydrogen deformation bands in the infrared. The ultraviolet band at 300 $m\mu$, which shifts to slightly higher wavelengths for methyl isomers, fortunately occurs in a region where analysis was unhindered by other components. For fluorene and 1-methylfluorene, analysis was straightforward, using specific absorptivity values of 59 and 41 respectively, determined at 300 $m\mu$ from available samples. The amount of the 2- and 3-methylfluorene mixture was determined at 260 $m\mu$ using an average specific absorptivity value of 116 obtained from pure samples.

Phenanthrenes. - Differentiation among the 1-methyl, 2-methyl, and 3-methyl isomers was readily made from strong infrared bands in the out-of-plane hydrogen deformation region at 11 to 14 μ . The strong ultraviolet band which ranged from 251 to 253.5 $m\mu$ in these CCD fractions indicated monomethyl-substituted phenanthrenes. This band shifts from 250.2 $m\mu$ for phenanthrene to a range of 251 to 254.4 $m\mu$ as observed in spectra of monomethylphenanthrenes. Dimethylphenanthrenes were also identified in the ultraviolet from the position of this strong band with a range of 252 to 256 $m\mu$. From literature spectra of 12 dimethylphenanthrenes this range was observed to be 252 to 258 $m\mu$. The shift in peak tubes accompanying the change in range of this ultraviolet band verified methylation. Phenanthrene determination was made in the ultraviolet, using a specific absorptivity value of 359 at 250.2 $m\mu$. An average specific absorptivity of 322 was determined from pure samples of 1-methyl-, 2-methyl-, and 3-methylphenanthrene. Absorbances were read from the peak of the large band as it shifted from 251 to 253.5 $m\mu$. The ratios of the individual monomethyl isomers were estimated from their strong infrared out-of-plane hydrogen deformation bands. For dimethylphenanthrenes, using the same intense ultraviolet band, an average specific absorptivity of 293 was determined from ultraviolet spectra of 12 dimethylphenanthrenes.

Anthracenes. - Qualitatively the distinction between anthracene and its monomethyl and dimethyl derivatives can best be made in the ultraviolet region where their longest wavelength bands are highly diagnostic. Neither the monomethyl nor the dimethyl anthracenes were substituted in the 9 or 10 position, as this causes a marked shift to longer wavelengths as compared to other positions. Quantitative analyses for anthracenes were conducted at 375.6 $m\mu$ for anthracene, 377.6 $m\mu$ for monomethylantracenes, and 380.0 $m\mu$ for dimethylantracenes. A specific absorptivity value of 43 for anthracene was determined from a pure sample. A monomethyl specific absorptivity value of 43 was obtained from a sample of 2-methylantracene and a literature spectrum of 1-methylantracene (15). From literature spectra of 7 dimethylantracenes, a value of 30 was determined for specific absorptivity.

Dibenzofurans. - Alkyldibenzofurans can be characterized in the infrared by a sharp, strong band in the 8.2 to 8.5 μ region (13) assigned to the C-O stretching vibration. The analysis was conducted in the ultraviolet region for dibenzofurans using a strong absorption band near 250 $m\mu$. For dibenzofuran a value of 115 at 248.8 $m\mu$ for the specific absorptivity was obtained from a pure sample. The monomethyldibenzofurans were determined by using an average specific absorptivity value of 98 at 251 to 253 $m\mu$, obtained from pure samples of 2-methyl-, 3-methyl-, and 4-methyldibenzofurans, and the spectrum for 1-methyldibenzofuran (14). For dimethyldibenzofurans, an average specific absorptivity value of 81 near 250 $m\mu$ was obtained from spectra of 6 dimethyldibenzofurans (14).

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TABLE 1. - Fractional distillation of neutral oils

CCD No.	Distillate fraction No.	Boiling range, ° C		Weight, grams
		10 mm	760 mm	
1	9	138 - 139	275 - 276	9.0
	10	139 - 141	276 - 278	9.0
2	11	141 - 143	278 - 280	8.6
	12	143 - 144	280 - 282	9.4
3	13	144 - 146	282 - 284	9.2
	14	146 - 148	284 - 286	9.3
4	15	148 - 149	286 - 287	9.6
	16	149	287	3.6
				¹ 67.7
		3.0 mm	760 mm	
5	1	123 - 125	287 - 290	1.9
	2	125 - 127	290 - 292	2.0
6	3	127 - 128	292 - 293	1.6
	4	128	293	1.7
7	5	128 - 132	293 - 298	1.7
	6	132 - 134	298 - 300	1.9
8	7	134 - 135	300 - 301	1.6
	8	135 - 136	301 - 302	1.9
	9	136 - 137	302 - 303	1.6
9	10	137 - 138	303 - 305	1.9
	11	138 - 143	305 - 310	2.0
10	12	143 - 144	310 - 311	2.1
	13	144 - 145	311 - 313	2.0
11	14	145 - 148	313 - 316	2.2
	15	148 - 150	316 - 318	2.3
	16	150 - 152	318 - 321	2.0
12	17	152 - 153	321 - 322	2.0
	18	153 - 160	322 - 329	1.9
13	19	160 - 167	329 - 337	1.9
14	20	167 - 171	337 - 342	2.0
	21	171 - 173	342 - 344	.5
				² 38.7

¹ Fractions 9 through 16 are 9.72 weight-percent of the total neutral oil.

² An aliquot representing 23.74 weight-percent of the total neutral oil.

TABLE 2. - Countercurrent distribution of high-boiling neutral oils

No.	Constituent Identity	Peak tube no.
<u>CCD NO. 1</u>		
1	Unknown I	34
2	Aliphatic carbonyl	58 FC
3	Dibenzofuran	44 FC
4	Acenaphthene	34 FC
5	Trimethylnaphthalenes (N ₁ , N ₂ , N ₃ , N ₄)	26 FC
6	Hydroaromatics, Biphenyls	14 FC
7	Alkylnaphthenes (6-membered ring)	10 FC
8	trans-Internal olefin	10.5 FC
9	Terminal olefin	10.5 FC
10	n-Alkane	9.0 FC
11	Branched-terminal olefin	8.5 FC
12	2-Methylalkane	6 FC
<u>CCD NO. 2</u>		
1	Unknown I	34.5
2	Aliphatic carbonyl	58 FC
3	Dibenzofuran	48 FC
13	Fluorene	44 FC
5	Trimethylnaphthalenes (N ₁ , N ₂ , N ₃ , N ₄)	25 FC
14	Tri- or tetramethylnaphthalenes (N ₅ , N ₆ , N ₇)	25 FC
6	Hydroaromatics, Biphenyls	14 FC
7	Alkylnaphthenes (6-membered ring)	10 FC
8	trans-Internal olefin	9 FC
9	Terminal olefin	9 FC
10	n-Alkane	8 FC
11	Branched terminal olefin	6 FC
12	2-Methylalkane	3.5 FC
<u>CCD NO. 3</u>		
15	o-Dimethylphthalate	4
1	Unknown I	33.5
2	Aliphatic carbonyl	58 FC
16	4-Methyldibenzofuran	48 FC
13	Fluorene	42 FC
14	Tri- or tetramethylnaphthalenes (N ₅ , N ₆ , N ₇)	26 FC

See footnotes at end of table.

Constituent		Peak tube no.
No.	Identity	
6	Hydroaromatics, Biphenyls	14 FC
7	Alkyl-naphthenes (6-membered ring)	10 FC
8	trans-Internal olefin	8 FC
9	Terminal olefin	8.5 FC
10	n-Alkane	8 FC
11	Branched-terminal olefin	8 FC
12	2-Methylalkane	5 FC
<u>CCD NO. 4</u>		
15	o-Dimethylphthalate	4
1	Unknown I	34
2	Aliphatic carbonyl	56 FC
16	4-Methyldibenzofuran	45 FC
13	Fluorene	42 FC
14	Tri- or tetramethylnaphthalenes (N ₅ , N ₆ , N ₇)	26 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	8 FC
9	Terminal olefin	8 FC
10	n-Alkane	7.5 FC
11	Branched terminal olefin	7 FC
12	2-Methylalkane	3 FC
<u>CCD NO. 5</u>		
17	Unknown II	34.5
2	Aliphatic carbonyl	56 FC
18	2-Methyldibenzofuran	² 36 FC
19	3-Methyldibenzofuran	² 36 FC
16	4-Methyldibenzofuran	² 36 FC
20	1-Methyldibenzofuran	² 36 FC
21	Tetramethylnaphthalenes	23 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	8 FC
9	Terminal olefin	8 FC
10	n-Alkane	8 FC
11	Branched-terminal olefin	7.5, 12 FC
12	2-Methylalkane	5 FC

See footnotes at end of table.

No.	Constituent Identity	Peak tube no.
<u>CCD NO. 6</u>		
17	Unknown II	36
18	2-Methyldibenzofuran	² 36 FC
19	3-Methyldibenzofuran	² 36 FC
16	4-Methyldibenzofuran	² 36 FC
20	1-Methyldibenzofuran	² 36 FC
21	Tetramethylnaphthalenes	24 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	8.5 FC
9	Terminal olefin	8.5 FC
10	n-Alkane	8.5 FC
11	Branched-terminal olefin	7.5 FC
12	2-Methylalkane	5 FC
<u>CCD NO. 7</u>		
17	Unknown II	35
22	Aliphatic carbonyl	55 FC
23	Unknown III	55 FC
24	Dimethyldibenzofuran	² 41 FC
18	2-Methyldibenzofuran	² 41 FC
19	3-Methyldibenzofuran	² 41 FC
20	1-Methyldibenzofuran	² 41 FC
25	1-Methylfluorene	38 FC
26	2- and/or 3-Methylfluorene	38 FC
27	Dimethyldibenzofurans	24 FC
21	Tetramethylnaphthalenes	23.5 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	8 FC
9	Terminal olefin	8 FC
10	n-Alkane	8 FC
11	Branched-terminal olefin	7 FC
12	2-Methylalkane	5 FC
<u>CCD NO. 8</u>		
17	Unknown II	35
28	Unknown IV	55 FC
29	Phenanthrene	51 FC
30	Unknown V	48 FC
18	2-Methyldibenzofuran	² 44 FC
19	3-Methyldibenzofuran	² 44 FC
25	1-Methylfluorene	38 FC
26	2- and/or 3-Methylfluorene	38 FC

See footnotes at end of table.

Constituent		Peak tube no.
No.	Identity	
31	2, 4-Dimethyldibenzofuran	31 FC
27	Dimethyldibenzofurans	24 FC
32	Alkylnaphthalenes (N ₈ , N ₉)	22.5 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	8 FC
9	Terminal olefin	8 FC
10	n-Alkane	8 FC
11	Branched-terminal olefin	7 FC
12	2-Methylalkane	5 FC
<u>CCD NO. 9</u>		
33	Carbazole	27
34	Unknown VI	37.5
29	Phenanthrene	51 FC
30	Unknown V	48 FC
35	Anthracene	48 FC
26	2- and/or 3-Methylfluorene	38 FC
31	Dimethyldibenzofuran (principally 2, 4-dimethyldibenzofuran)	30 FC
32	Alkylnaphthalenes (N ₈ , N ₉)	22 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	7 FC
9	Terminal olefin	7 FC
10	n-Alkane	7 FC
11	Branched-terminal olefin	7 FC
12	2-Methylalkane	4 FC
<u>CCD NO. 10</u>		
33	Carbazole	27
34	Unknown VI	38
29	Phenanthrene	51 FC
30	Unknown V	48 FC
35	Anthracene	47 FC
36	Carbonyl compound	42 FC
31	Dimethyldibenzofurans (principally 2, 4-dimethyldibenzofuran)	32.5 FC
32	Alkylnaphthalenes (N ₈ , N ₉)	22 FC
6	Hydroaromatics, Biphenyls	13 FC
8	trans-Internal olefin	7 FC
9	Terminal olefin	7 FC
10	n-Alkane	7 FC
11	Branched-terminal olefin	7, 10 FC
12	2-Methylalkane	4 FC

Constituent		Peak tube no.
No.	Identity	
<u>CCD NO. 11</u>		
33	Carbazole	27
34	Unknown VI	39
37	Unknown VII	54 FC
29	Phenanthrene	51 FC
30	Unknown V	48 FC
35	Anthracene	45 FC
38	2-Methylphenanthrene	43 FC
39	3-Methylphenanthrene	41 FC
40	1-Methylphenanthrene	38 FC
41	Dimethyldibenzofurans	30 FC
42	Alkylnaphthalenes (N ₁₁ , N ₁₀)	21 FC
6	Hydroaromatics, Biphenyls	13 FC
8	trans-Internal olefin	7 FC
9	Terminal olefin	7 FC
10	n-Alkane	7 FC
11	Branched-terminal olefin	7, 10 FC
12	2-Methylalkane	4 FC
<u>CCD NO. 12</u>		
43	1-Methylcarbazole	² 26.5
33	Carbazole	² 26.5
44	Unknown VIII	42
35	Anthracene	45 FC
38	2-Methylphenanthrene	² 40 FC
39	3-Methylphenanthrene	² 40 FC
40	1-Methylphenanthrene	² 40 FC
45	1- and/or 2-Methylanthracene	40 FC
41	Dimethyldibenzofurans	28 FC
42	Alkylnaphthalenes (N ₁₁ , N ₁₀)	18.5 FC
6	Hydroaromatics, Biphenyls	11 FC
8	trans-Internal olefin	6, 9.5 FC
9	Terminal olefin	6 FC
10	n-Alkane	7 FC
11	Branched-terminal olefin	6, 9 FC
12	2-Methylalkane	4.5 FC
<u>CCD NO. 13</u>		
46	2- and/or 3-Methylcarbazole	² 29
43	1- and/or 4-Methylcarbazole	² 29
47	Unknown IX	46
38	2-Methylphenanthrene	² 40 FC

See footnotes at end of table.

Constituent		Peak
No.	Identity	tube no.
39	3-Methylphenanthrene	² 40 FC
40	1-Methylphenanthrene	² 40 FC
45	1- and/or 2-Methylanthracene	38 FC
48	Alkyldibenzofurans	26 FC
42	Alkyl-naphthalenes (N ₁₁ , N ₁₀)	18.5 FC
6	Hydroaromatics, Biphenyls	11 FC
8	trans-Internal olefin	7 FC
9	Terminal olefin	7 FC
10	n-Alkane	6 FC
11	Branched-terminal olefin	7 FC
12	2-Methylalkane	4 FC
<u>CCD NO. 14</u>		
46	2- and/or 3-Methylcarbazole	² 31
43	1- and/or 4-Methylcarbazole	² 31
47	Unknown IX	46
49	Unknown X	57 FC
45	1- and/or 2-Methylanthracene	39 FC
50	Dimethylphenanthrenes	35.5 FC
51	Dimethylanthracenes	32 FC
48	Alkyldibenzofurans	25 FC
42	Alkyl-naphthalenes (N ₁₁ , N ₁₀)	18 FC
6	Hydroaromatics, Biphenyls	11 FC
8	trans-Internal olefin	6 FC
9	Terminal olefin	6 FC
10	n-Alkane	6 FC
11	Branched-terminal olefin	6 FC
12	2-Methylalkane	3 FC

¹ FC = fraction collector.

² Peak tube for a mixture of compounds.

TABLE 3. - Quantitative analysis of neutral oils
boiling from 275° to 344° C

Constituent	Weight-percent in neutral oil ¹
Alkylbinuclear naphthenes	0.15
n-Alkanes	3.16
2-Methylalkanes	1.09
Terminal olefins	2.42
Branched-terminal olefins	.37
trans-Internal olefins	1.29
Aliphatic carbonyl	.21
	8.69
Acenaphthene	.37
Hydroaromatics, biphenyls	3.02
Trimethylnaphthalene, No. 5	1.88
Alkyl-naphthalenes (tetramethyl), No. 14	2.60
Alkyl-naphthalenes, Nos. 21, 32, 42	7.75
	12.23
Fluorene	.20
1-Methylfluorene	.10
2- and/or 3-Methylfluorene	.23
	.53
Phenanthrene	.39
1-Methylphenanthrene	.11
2-Methylphenanthrene	.19
3-Methylphenanthrene	.23
Dimethylphenanthrenes	.23
	1.15
Anthracene	.05
Monomethylantracenes	.04
Dimethylantracenes	.01
	.10

¹ Total neutral oil (distilling up to about 360° C) constituted 16.92 weight-percent of the total tar.

(Continuing)
TABLE 3. - Quantitative analysis of neutral oils
boiling from 275° to 344° C

Constituent	Weight-percent in neutral oil ¹
Dibenzofuran	0.32
1-Methyldibenzofuran	.19
2-Methyldibenzofuran	.27
3-Methyldibenzofuran	.46
4-Methyldibenzofuran	.34
Dimethyldibenzofurans	3.84
(Approximately 50 percent 2, 4-dimethyldibenzofuran)	
Alkylated dibenzofurans (trimethyl-)	.68
	<hr/> 6.10
o-Dimethylphthalate	.03
Carbazole	.09
1- and/or 4-Methylcarbazole	.08
2- and/or 3-Methylcarbazole	.17
	<hr/> .17
Unknowns I through X	1.02

¹ Total neutral oil (distilling up to about 360° C) constituted 16.92 weight-percent of the total tar.

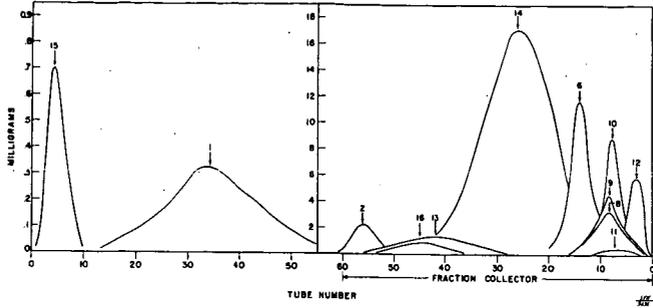


FIGURE 1. - Countercurrent Distribution of Neutral Oil, Run No. 4.

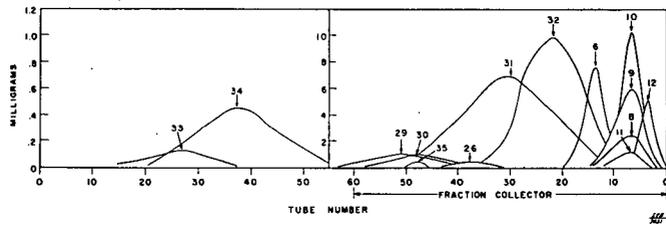


FIGURE 2. - Countercurrent Distribution of Neutral Oil, Run No. 9.

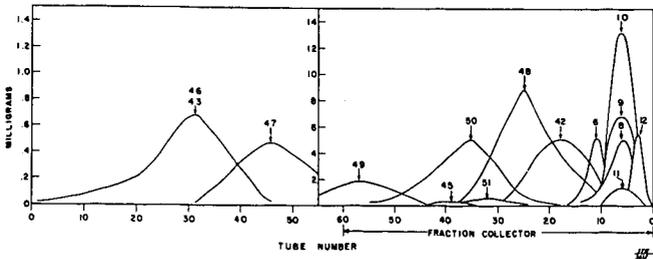


FIGURE 3. - Countercurrent Distribution of Neutral Oil, Run No. 14.

FORMATION AND NATURE OF NITROGENOUS GUM DERIVED FROM
COKE-OVEN GAS UNDER CRYOGENIC CONDITIONS

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Introduction

A type of nitrogenous gum called "vapor-phase gum" has long been known to form in coke-oven gas. It is generally accepted that the formation of this gum is due primarily to the interaction of nitric oxide (NO), oxygen, and organic compounds such as the unsaturated hydrocarbons. Another type of nitrogenous gum is one that is formed in coke-oven gas under cryogenic conditions that also involves the interaction of nitric oxide, oxygen, and hydrocarbons. It is widely recognized^{1,2,3,4}* that NO by itself does not react with gum-forming hydrocarbons; however, under cryogenic conditions the oxidation of NO or its dimer, (NO)₂, is rapid and the products of the oxidation, nitrogen trioxide (N₂O₃) and nitrogen tetroxide (N₂O₄), react with gum-forming hydrocarbons. In the liquid phase, ethylene is known to react with N₂O₃ and N₂O₄; however, such reactions are slow at low temperatures.^{1,5} Generally it is assumed that nitrogen oxides react primarily with cyclopentadiene and butadiene when present in liquid ethylene. It is the purpose of this paper to present the results of work undertaken to investigate the reactions, and the products of the reactions, of N₂O₃ and N₂O₄ with cyclopentadiene and butadiene in liquid ethylene. For comparison, some investigations were made in which liquid ethane was used in place of liquid ethylene.

Materials and Experimental Work

Materials - All materials were obtained from The Matheson Company. Ethylene (99.5% minimum purity) and ethane (99.0% minimum) were purified by passage through activated carbon. Butadiene and N₂O₃ (both 99.0% minimum purity) and N₂O₄ (99.5% minimum) were used as received. Cyclopentadiene was freshly distilled as needed; mass-spectrometric analysis of the distilled material showed it to contain 93.8 percent cyclopentadiene, 2.7 percent dicyclopentadiene, 2.9 percent 1,3-cyclohexadiene, 0.5 percent benzene, and less than 0.1 percent toluene.

Apparatus and Procedure - Liquid ethylene (or ethane) for the tests was prepared by passing the Matheson gas through activated

* See References.

carbon and condensing it at atmospheric pressure and, as well as possible, in the absence of air. As the first step in preparing the gums, the Pyrex condenser and receiver were purged with gaseous ethylene (or ethane) and the receiver was cooled with liquid nitrogen. When cyclopentadiene was used, a weighed amount of the diene was injected into the receiver through a septum-covered port by means of a syringe and about 200 cubic centimeters (cc) of liquid ethylene (or ethane) were then condensed into the receiver. When butadiene was used, it was more convenient to condense the liquid ethylene (or ethane) into the receiver first and then inject a measured volume of butadiene gas into the liquid by means of a graduated syringe. With either procedure, the next step was to introduce a measured volume of N_2O_3 or N_2O_4 into the liquid with a graduated syringe. The following procedure was followed to minimize the amount of nitrogen oxide that escaped as vapor during this operation. The syringe tip (a polyethylene tube) was inserted into the liquid and a small portion of liquid was withdrawn into the partially filled syringe containing nitrogen oxide; this liquid vaporized and expelled the nitrogen oxide from the syringe. The operation was repeated several times to ensure that all of the nitrogen oxide was flushed into the receiver. (With ethylene, the temperature of the reaction mixture was about $-105^\circ C$; with ethane, the temperature of the reaction mixture was about $-90^\circ C$.) After 15 minutes in the receiver, the mixture was placed in a loosely covered vessel and left to stand until the liquid evaporated (about 1 hour).

For colorimetric examinations, the gums remaining after evaporation of the reaction mixtures were weighed and then dissolved in 20 milliliters (ml) of a 1 percent aqueous solution of sodium hydroxide. The solutions were allowed to stand 20 to 30 minutes for color development, and the spectral absorbance was then measured at a wavelength of 425 millimicrons on a Beckman Model DU spectrophotometer. With some solutions, the optical densities were too high to be measured and dilution with known amounts of additional caustic was necessary.

For infrared measurement, the gum residue was mounted on a sodium chloride plate immediately after it was isolated, and its spectrum from 2 to 15 microns was obtained. Infrared measurements were also repeated after the gum residues had been stored for varying numbers of days on the plates.

For determination of the nitrogen content of a gum residue, the gum was first allowed to stand overnight. On the following day, the weight of the gum was determined and the gum was dissolved by adding dilute (1%) aqueous sodium hydroxide to the vessel. The gum in the caustic solution was then reduced with Devarda's metal and subsequently analyzed for nitrogen by the Kjeldahl method.

Results and Discussion

Gums were formed rapidly when N_2O_3 and either butadiene or cyclopentadiene were introduced into liquid ethylene; however, the

yields of gum varied considerably with differences in the mole ratio of N_2O_3 to butadiene. In fact, difficulties were encountered in reproducing the yield of gum with any particular mole ratio of reactants. Variations were most noticeable with the reaction mixtures prepared with butadiene. Because of such variations, the reaction mixtures in which this compound had been introduced were divided into aliquots so that multiple determinations of the gum content could be made. The variability in the yield of gum might be explained if the initial products formed from the reactants can either evaporate or polymerize into the non-volatile gum.

In an attempt to develop a method for quantitative determination of the gums, aqueous sodium hydroxide solutions of gums were prepared and examined spectrophotometrically. The absorbance of light of 425-millimicron wavelength (selected from an examination of the absorption spectra of such solutions) was found to be roughly proportional to the concentration of the gum, Figure 1. As the ratio of nitrogen oxide to diene was increased, however, the slopes of the Beer's law plots shifted markedly and irregularly, Figures 1 and 2. The technique therefore could not be used to estimate gum concentrations.

Significantly more gum was obtained from cyclopentadiene than from butadiene. For example, at a ratio of about 0.75 moles of N_2O_3 per mole of diene (in liquid ethylene) cyclopentadiene yielded about 0.5 grams of gum per gram of diene whereas butadiene yielded only about 0.1 grams. One possible reason for this difference may be that the products of the reaction with cyclopentadiene are less volatile and tend to remain as residue upon evaporation of the ethylene.

As shown in Figure 3, air appeared to retard the gum formation when N_2O_3 and cyclopentadiene were introduced into liquid ethylene, since greater yields of gum were obtained when air was excluded from the reaction mixtures. It may be that air oxidizes the N_2O_3 to N_2O_4 , which is less reactive as a gum former.

Participation of Ethylene in Gum Formation

Under the conditions of the described tests, no gums were formed when only N_2O_3 was added to liquid ethylene. Nevertheless, ethylene was found to take part in the gum formation when both N_2O_3 and cyclopentadiene were introduced into liquid ethylene.

When the amount of N_2O_3 charged was in considerable excess of the amount of cyclopentadiene, the yield of gum was considerably greater than the amount of cyclopentadiene charged, Figure 4. The nitrogen content of such gums was only 6.7 to 7.8 percent, however, indicating that N_2O_3 did not comprise the major portion of the gum. It was therefore apparent that the gum contained ethylene, and because of the participation of ethylene, the yields of gum were not limited by the amounts of dienes available.

Because ethane was not expected to react with the gum-formers

at the temperatures employed (about -100°C), several tests were made in which the nitrogen oxide and diene were mixed with liquid ethane instead of liquid ethylene. Comparison of the results of these tests with the results obtained with ethylene gave further evidence that ethylene participated in gum formation.

Plots of the yields of gum per gram of cyclopentadiene charged against the starting reactant ratios are shown in Figure 5. In liquid ethane, the highest yield of gum per gram of cyclopentadiene was obtained when near equimolecular amounts of N_2O_3 and cyclopentadiene were used, and in contrast to the results obtained with liquid ethylene, the yield of gum per gram of cyclopentadiene subsequently decreased as the proportion of cyclopentadiene charged was decreased. Thus, the divergence of the curves for the gum yields per gram of cyclopentadiene in the two liquids indicates that ethylene was incorporated in the gum. As illustrated by the curves presented in Figure 6, the gum yields per gram of N_2O_3 charged also appeared to differ somewhat in the two media.

Gum Formation From the Addition of N_2O_4 and Cyclopentadiene to Liquid Ethylene

Gums were also formed when N_2O_4 and cyclopentadiene were added to liquid ethylene, Figure 7. The gum-forming reaction was similar to that obtained with N_2O_3 in that gum of about the same nitrogen content was produced and at least some and probably all, of the gums contained ethylene; however, the gum yields were somewhat smaller.

The gum produced from N_2O_4 and cyclopentadiene in ethylene contained 5.8 to 7.1 weight percent nitrogen, which was about the same as for the gums produced from N_2O_3 and cyclopentadiene in ethylene (6.7 to 7.8 wt %). That the gum formed from N_2O_4 contained ethylene was evident from the fact that the yields of gum at the higher N_2O_4 -to-cyclopentadiene ratios tested were unusually high for the amounts of cyclopentadiene charged and, as shown by the nitrogen content of the gums, these unusually high yields could not be accounted for by the proportion of N_2O_4 incorporated in the gum. Regardless of the ratios of N_2O_4 to cyclopentadiene, the gums all contained about the same percentage of nitrogen.

The gum yields with N_2O_4 were somewhat less than with N_2O_3 , as indicated by experiments in which gums were produced with the two nitrogen oxides by procedures made as identical as possible. By starting with 1.5 moles of the nitrogen oxide per mole of cyclopentadiene, the yield of gum per gram of cyclopentadiene was about 1.5 grams with N_2O_3 and about 1.2 grams with N_2O_4 .

Infrared Examination of Gums

Infrared spectra were obtained for 13 samples of gum produced

by mixing cyclopentadiene and N_2O_3 with liquid ethylene. That the spectra are those of a highly unstable gum was confirmed when one of the freshly isolated samples "fumed-off" after it was placed on a sodium chloride plate for infrared examination. Typical spectra are shown in Figures 8, 9, and 10 for gums produced from N_2O_3 -to-cyclopentadiene mole ratios of 0.52, 2.3, and 7.7, respectively.

In the spectra of the gum, characteristic absorptions were noted for several groups of atoms. Evidence of the following groups was obtained in all gum samples:

- (1) -OH or -NH (possibly representing hydrogen bonding).
- (2) -CH (merely indicating carbon-hydrogen linkages in general).
- (3) C=O (shifted in concentration and structure during storage of samples).
- (4) -ONO₂ (definitely organic nitrate).
- (5) -CNO₂ (organic nitro groups).
- (6) NaNO₃.

The same identifications were also made in samples prepared by passing N_2O_3 through cyclopentadiene in the absence of ethylene; however, the residue from the evaporation of ethylene treated with N_2O_3 in the absence of cyclopentadiene showed only the NaNO₃ absorption. NaNO₃ is probably present in all of the samples because of a reaction of nitrogen oxides with the salt plate in the presence of moisture.

The functional groups whose presence was detected (carbonyl, nitro, and nitrate) or suspected (hydroxyl) in the gum were among those found by Levy and co-workers⁵⁾ in the products of the reaction of N_2O_3 and N_2O_4 with simple olefins at 0 C. According to Levy, when N_2O_3 and an unsaturated compound are reacted, the primary reaction is a simple addition to yield products (usually several) containing nitro (-NO₂), nitrite (-ONO), and nitroso (-NO) groups. Products containing nitrite and nitroso groups are seldom isolated, apparently because of their instability (if isolated from solution they usually explode) and ensuing secondary reactions. Nitrite groups are frequently oxidized by N_2O_4 to nitrate groups; however, they may also be hydrolyzed (for example, by water produced by oxidation) to produce hydroxyl groups and nitric or nitrous acid. The fate of nitroso groups is not known. Carbonyl groups might be expected to result from the nitrogen oxide oxidation of carbons having nitro groups.

* * *

In summary, the experimental investigations have confirmed that nitrogenous gums are formed when N_2O_3 or N_2O_4 and cyclopentadiene or butadiene are introduced into liquid ethylene. Indications were obtained that ethylene is readily incorporated in the gum. Some of the reaction products are apparently volatile; however, other material formed remains as a gummy residue when the solvent ethylene is evaporated. Whereas the yields of gum per unit weight of diene increase

with an increase in the ratio of N_2O_3 to diene, the nitrogen content of the gum prepared from N_2O_3 and cyclopentadiene in ethylene was 5.8 to 7.1 weight percent, regardless of the starting reactant ratio. Furthermore, the yields were not limited by the amount of diene present but only by the amount of nitrogen oxide available. The yields of gum residue were greater with cyclopentadiene than with butadiene and the yields appeared to be favored by the absence of air. It may be that air oxidizes N_2O_3 to N_2O_4 , which is less reactive as a gum former. Infrared studies have shown what functional groups are present in the gum, and the spectra obtained should be useful as references in examining materials formed under similar conditions.

Acknowledgement

The authors wish to acknowledge the assistance of A. J. Miskalis, who measured and interpreted the infrared spectra of the gum samples, R. W. Baudoux, who determined their nitrogen content, and Dr. M. H. Wilt, for helpful suggestions during the work and for reviewing the manuscript.

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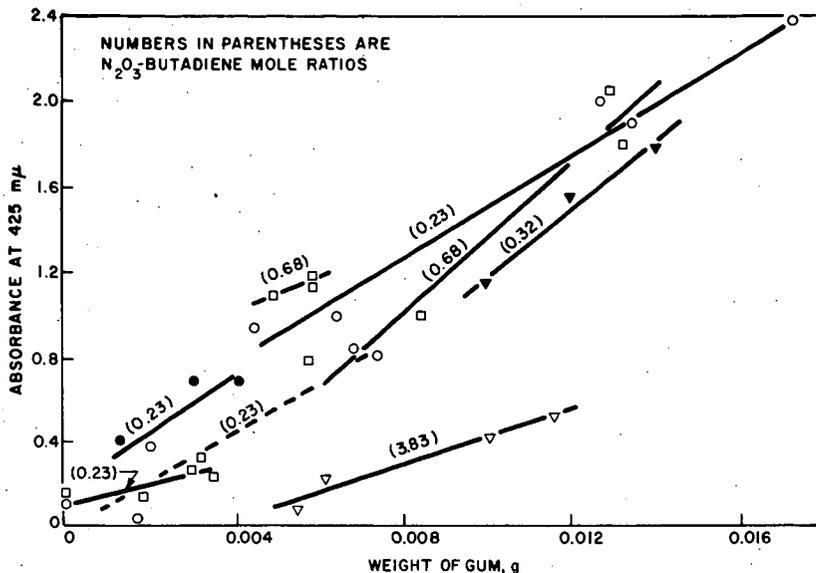


Fig. 1.-SPECTRAL ABSORBENCE OF CAUSTIC SOLUTIONS OF GUMS PREPARED FROM NITROGEN TRIOXIDE AND BUTADIENE IN LIQUID ETHYLENE

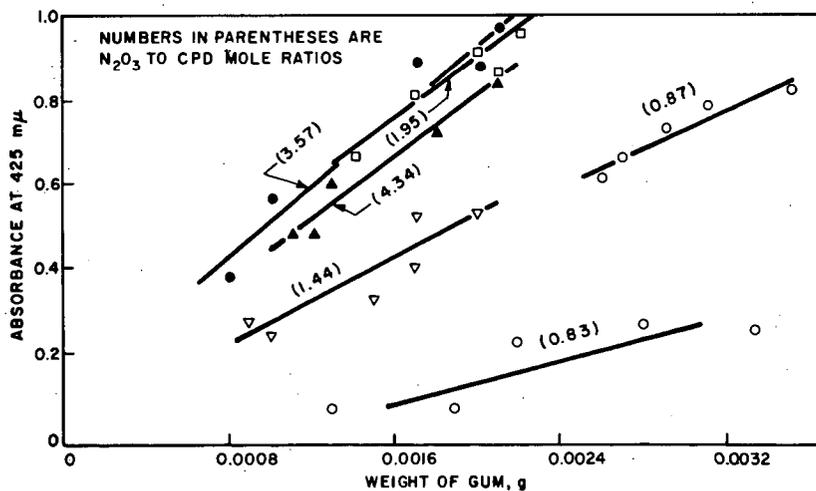


Fig. 2.-SPECTRAL ABSORBENCE OF CAUSTIC SOLUTIONS OF GUMS PREPARED FROM CYCLOPENTADIENE AND N_2O_3 IN ETHYLENE

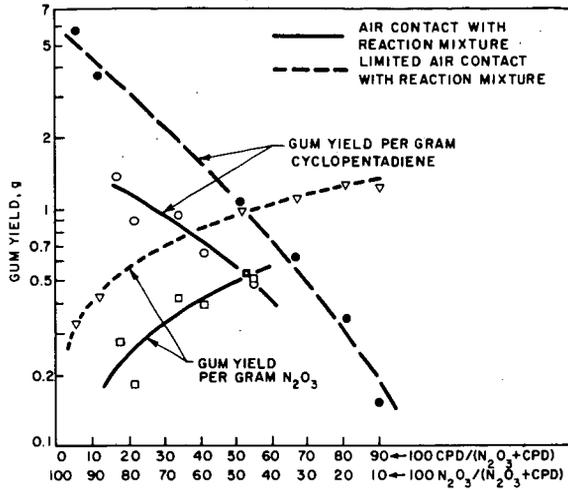


Fig. 3.-YIELDS OF GUM FROM DIFFERENT N₂O₃ TO CYCLOPENTADIENE RATIOS (IN LIQUID ETHYLENE)

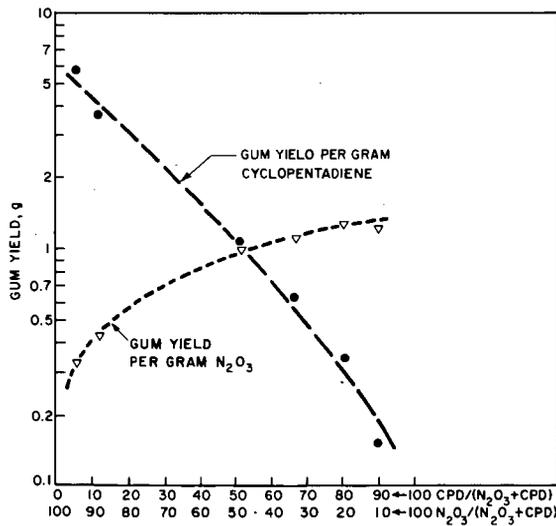


Fig. 4.-YIELDS OF GUM FROM DIFFERENT N₂O₃ TO CYCLOPENTADIENE RATIOS (IN LIQUID ETHYLENE)

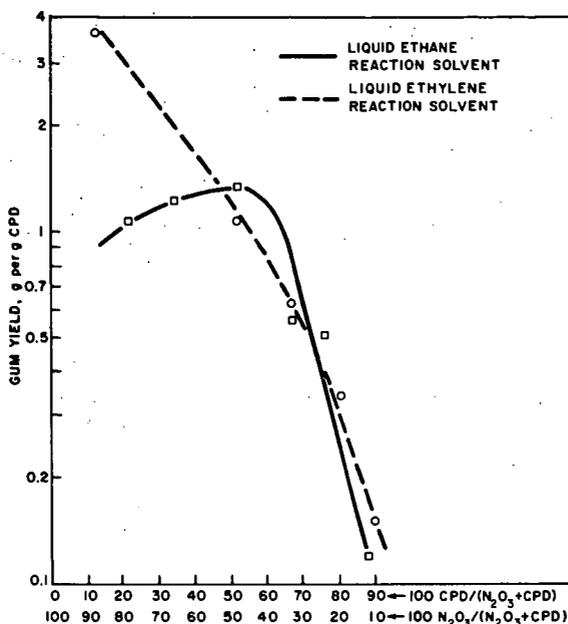


Fig. 5.-YIELDS OF GUM FROM DIFFERENT N_2O_3 TO CYCLOPENTADIENE RATIOS

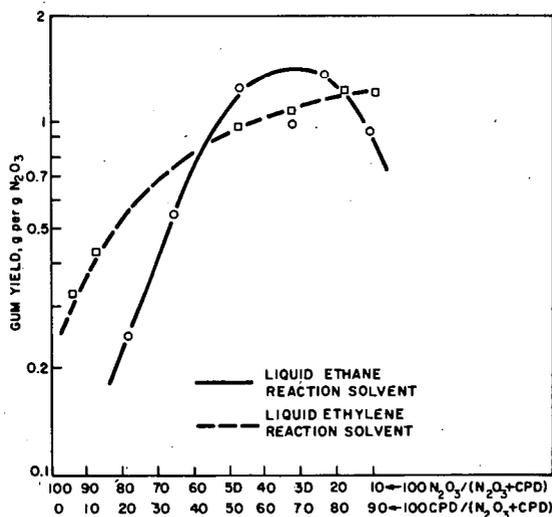


Fig. 6.-YIELDS OF GUM FROM DIFFERENT N_2O_3 TO CYCLOPENTADIENE RATIOS

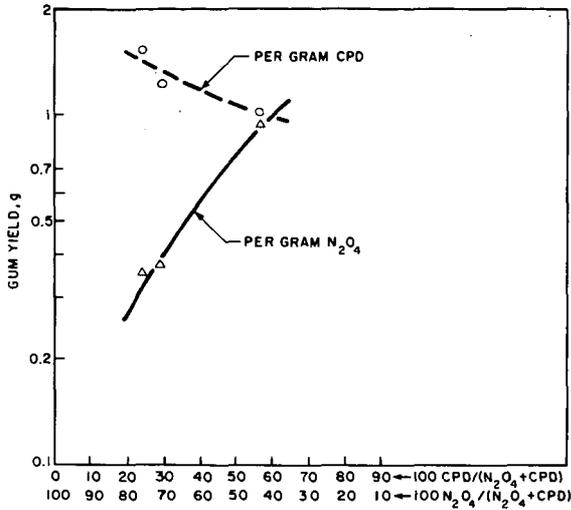


Fig. 7.-YIELDS OF GUM FROM DIFFERENT N₂O₄ TO CYCLOPENTADIENE RATIOS

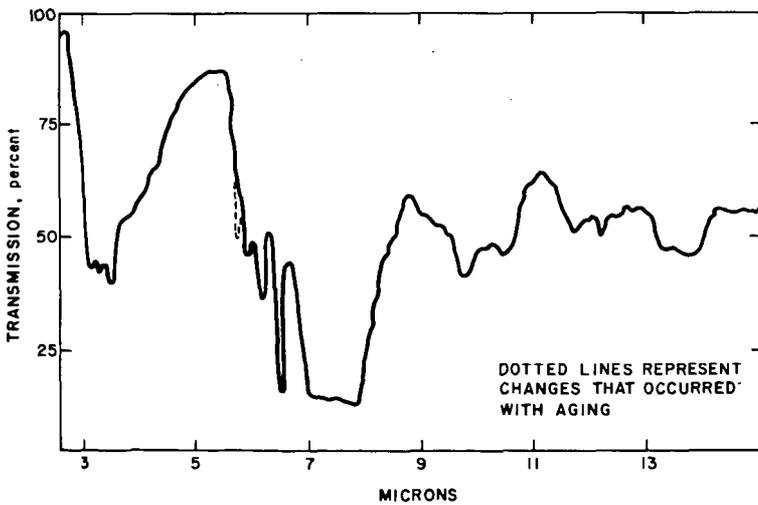


Fig. 8.-INFRARED SPECTRUM OF GUM PRODUCED FROM THE REACTION OF N₂O₃ AND CYCLOPENTADIENE IN ETHYLENE (0.52 MOLE N₂O₃ PER MOLE OF CYCLOPENTADIENE)

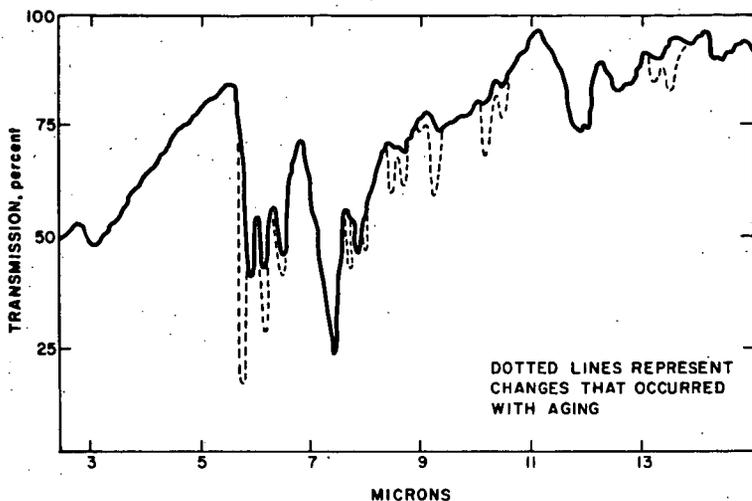


Fig. 9.-INFRARED SPECTRUM OF GUM PRODUCED FROM THE REACTION OF N_2O_3 AND CYCLOPENTADIENE IN ETHYLENE (2.30 MOLES N_2O_3 PER MOLE OF CYCLOPENTADIENE)

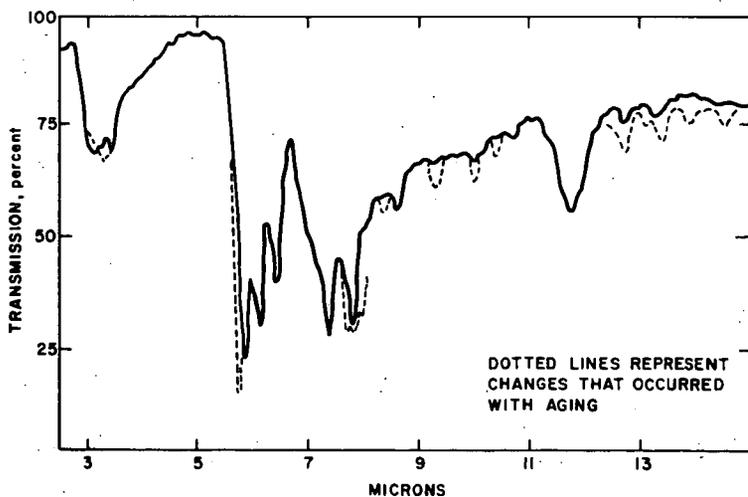


Fig. 10.-INFRARED SPECTRUM OF GUM PRODUCED FROM THE REACTION OF N_2O_3 AND CYCLOPENTADIENE IN ETHYLENE (7.73 MOLES N_2O_3 PER MOLE OF CYCLOPENTADIENE)

HOT GAS IGNITION TEMPERATURES OF HYDROCARBON FUEL VAPOR-AIR MIXTURES

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ABSTRACT

Laminar hot air jets of 1/4 to 3/4-inch diameter were employed to determine the hot gas ignition temperatures of various combustible vapor-air mixtures. The combustibles were n-hexane, n-octane, n-decane, a hydrocarbon jet fuel (JP-6) and an adipate ester aircraft engine oil (MIL-L-7808). Minimum ignition temperatures occurred at a fuel-air weight ratio of about 0.5 and were not greatly sensitive to variations of fuel concentration. Moderate variations of jet velocity also had little influence on these ignition temperatures. However, these temperatures decreased with an increase in heat source dimensions (jet diameter) similar to that observed in the hot surface ignition of the hydrocarbon combustibles. Furthermore, it was noted that the hot gas ignition temperatures of the combustibles tended to approximate corresponding auto-ignition and wire ignition temperatures when the size of the heat source and the ignition criterion were the same. Temperature profiles obtained for 1/2-inch diameter hot air jets indicated that the jet temperatures required to produce "hot" flame ignitions and luminous or "cool" flame reactions with these combustibles are of greater significance than the corresponding heat flux values.

INTRODUCTION

Most of the ignition temperature data available for combustible fluids have been obtained using heated vessels, wires, or tubes as the sources of ignition. A jet of heated air or other gas, if sufficiently hot, can also produce ignition when it comes into contact with combustible gases or vapors. Such an ignition source may be a problem during the rupture of an oil seal in a jet engine or during blasting operations in a coal mine where hot gases are released from the explosives employed. The temperatures at which combustible gas mixtures can be ignited by laminar jets of hot air and inert gases have been determined only in recent years by Wolfhard and others (5,6,7) for hydrogen, carbon monoxide, and various low molecular weight hydrocarbons. The present work was conducted to investigate the hot gas (air) ignition temperature characteristics of several high molecular weight hydrocarbon combustibles mixed with air.

Hot gas ignitions differ from wire ignitions and autoignitions in heated vessels primarily in that surface effects are absent with a hot gas heat source, providing the reaction chamber is relatively large. The hot gas ignition temperatures of hydrocarbon combustible mixtures have been reported to agree generally with corresponding wire ignition temperatures but to be much higher than the autoignition temperatures (AIT's) of the mixtures (7). However, according to our hot surface ignition studies (2) and to the preliminary findings of the present study (3) which are included here, the variation between such ignition temperatures can depend greatly on the size of the heat source and on the ignition criterion used. The hot gas ignition temperature data of this work were obtained with laminar jets of hot air injected into combustible vapor-air mixtures under near-stagnant flow conditions. Data are included on the effects of combustible concentration, jet diameter, and jet velocity for a given size of reaction chamber. Since a relatively stable luminous jet is ordinarily observed prior to these ignitions, temperature profiles of the jets were obtained to compare the heat requirements for the initial luminous or "cool" flame reactions and the

subsequent "hot" flame ignitions with each combustible. The combustibles included n-hexane, n-octane, n-decane, a hydrocarbon jet fuel (JP-6), and an adipate ester aircraft engine oil (MIL-L-7808).

EXPERIMENTAL APPARATUS AND PROCEDURES

The apparatus used for the hot gas ignition temperature determinations is shown in figure 1 and, except for some minor modifications, is similar to that employed by Wolfhard (7). Basically, the apparatus consisted of a tubular ceramic furnace that was used to heat the air stream, a cylindrical reaction chamber into which was fed the hot air jet and the combustible vapor-air mixture, and the feed assemblies that provided the desired mixture at a uniform rate. The tubular furnace was wound externally with platinum-rhodium wire and was enclosed in a cylindrical Nichrome*-wound furnace (3-inch ID). The reaction chamber consisted of a 4-inch diameter Pyrex pipe (26 inches long) that was also heated to maintain the combustible mixture at a given temperature. Narrow slits were located on both sides of the enclosed pipe along its longitudinal axis to permit visual observation of flame propagation. The combustible mixture was fed to the reaction chamber through a "mixing ring" (perforated coil of tubing) located just below the base of the hot jet; a water jacket between the ring and the ceramic tubular furnace helped maintain the mixture at a uniform initial temperature.

The temperatures of the hot air jets were measured with a 33-B&S gage platinum/platinum-10 percent rhodium thermocouple at a point of about 1/4 inch above the jet base; the temperature decreased progressively with the height above the jet base at a rate that was determined in part by the jet diameter and velocity. The temperatures of the combustible mixtures were measured with three thermocouples spaced 3 inches apart as shown in figure 1; recorded temperature differences were usually not in excess of $\pm 25^\circ$. A mixture temperature of 600° F was used for the engine oil which contained higher boiling point constituents than did the fuels. The mixture flow rate was $365 \text{ in}^3/\text{min}$ ($\sim 1 \text{ in}/\text{sec}$), and the jet flow rate was $185 \text{ in}^3/\text{min}$ ($\geq 50 \text{ in}/\text{sec}$), both at N.T.P. conditions, in the experiments with 1/4, 3/8, and 1/2-inch diameter jets; a jet flow rate of $365 \text{ in}^3/\text{min}$ ($\sim 50 \text{ in}/\text{sec}$) was used with a 3/4-inch size jet. These jet flow rates were used since they appeared to be optimum for ignition of the mixtures in the 4-inch diameter reaction chamber.

To conduct an experiment, the temperatures of the hot air jet and ambient atmosphere in the reaction chamber were measured initially. The thermocouples were then removed and the combustible mixture was introduced, flowing coaxially with the hot jet. If ignition did not occur, the jet temperature was increased in successive increments until ignition was evidenced by the propagation of flame throughout the combustible mixture. Normally, a small precursor flame or luminous column was faintly visible above the base of the jet prior to ignition (figure 2); this flame extended to a height of 6 inches or less above the jet base and resembled a pale blue "cool" flame. Fuel residence time and fuel-air ratio were also varied to obtain the minimum ignition temperatures with each size of hot air jet. Generally, ignitions occurred in 10 to 60 seconds, although a few took place after as much as 180 seconds from the time the combustible mixture was admitted. The minimum ignition temperature values were repeatable to within $\pm 25^\circ$.

Temperature profiles of 1/2-inch diameter jets of hot air were determined with the jets flowing into preheated air and into preheated combustible vapor-air mixtures. For this purpose, the cylindrical reaction chamber was equipped with a probe which

* Reference to trade names is for information only and endorsement by the Bureau of Mines is not implied.

could be adjusted to make axial and radial temperature measurements at various heights within the hot gas jet. Adjustment of the temperature probe was made by rotating a micrometer in contact with a movable plate supporting the probe. The thermocouple bead of this probe was made with 36-gage platinum/platinum-rhodium wire and was coated with a ceramic material recommended by the Bureau of Standards; addition of the coating resulted in slightly lower ($\leq 25^\circ$) jet temperatures. In making these measurements, jet base temperatures were selected to produce the initial luminous reactions and the subsequent "hot" flame ignitions under the given flow conditions. However, the ignition reactions were usually quenched when the temperature probe was inserted at a distance between 0 and 4 inches above the jet base; under such conditions, ignitions were obtained only when the probe was positioned at distances in excess of about 4 inches above the base of the jet.

All of the neat hydrocarbon fuels used in this work were of chemically pure grade, at least 99 percent pure. The MIL-L-7808 engine oil consisted primarily of adipate diesters which vaporized at temperatures between 480° and 780° F; its flash point was 435° F. The JP-6 jet fuel contained about 85 percent saturated hydrocarbons and 14 percent aromatic hydrocarbons; its flash point was 100° F.

RESULTS AND DISCUSSION

Hot Gas Ignition Temperatures

The temperature required to ignite a combustible vapor-air mixture with a jet of hot gas depends on the dimensions of the jet as well as on the composition and velocity of the jet and combustible mixture. Since jets of hot air were used in the present work, the combustible vapor-air mixture was diluted by the air jet, particularly along the interface between the two moving fluids. Accordingly, relatively high fuel concentrations and low jet flow rates should be the most optimum for ignition; low flow rates provide low air dilution rates and long contact times with the combustible which are highly favorable for ignition. The results presented here for n-hexane, n-octane, n-decane, JP-6 jet fuel, and MIL-L-7808 engine oil vapor-air mixtures were consistent in this connection.

Figure 3 shows the variation of the hot gas ignition temperatures with fuel-air weight ratio (F/A) employing 1/2-inch diameter air jets flowing concurrently into the combustible vapor-air mixtures; jet flow rate was $185 \text{ in}^3/\text{min}$, and the mixture flow rate was $365 \text{ in}^3/\text{min}$. As in hot surface ignition temperature determinations (2), the effect of F/A ratio is seen to be slight except at low ratio values (~ 0.30) where the ignition temperatures tend to increase noticeably as the F/A ratio is decreased. Similar behavior was also noted in the ignition temperature determinations made with 1/4, 3/8 and 3/4-inch diameter hot air jets; figure 4 shows the data obtained for n-decane with the various sized jets. Generally, a F/A ratio of approximately 0.5 was required to obtain the minimum temperatures for ignition. Since uniform mixtures of these combustibles in air usually would not be expected to propagate flame at such high F/A ratios, the observed behavior is probably attributed to the dilution of the mixtures and the elevation of the mixture temperatures ($\geq 350^\circ$ F) by the hot air jet.

In the above experiments, with the 1/2-inch diameter jet the jet velocity was about $50 \text{ in}/\text{sec}$ ($185 \text{ in}^3/\text{min}$) and the mixture velocity $1 \text{ in}/\text{sec}$ ($365 \text{ in}^3/\text{min}$). Data obtained under other flow conditions are summarized in table 1 from experiments conducted with 1/2-inch diameter jets of hot air and MIL-L-7808 engine oil vapor-air mixtures. It is evident from these data that the influence of jet velocity on minimum ignition temperature was not great for the range of velocities used in these experiments; this behavior is consistent with that reported by other investigators (5). The ignition temperature increased only slightly when the jet velocity was varied from 36.5 to $81.0 \text{ in}/\text{sec}$ with a constant mixture velocity of $1.0 \text{ in}/\text{sec}$. They also

increased slightly when the mixture velocity was varied between 0.7 and 1.5 in/sec; here, the jet velocity/mixture velocity ratio was maintained at a constant value slightly above 50. Although a jet velocity of approximately 50 in/sec was near optimum for ignition of the mixtures with 1/2-inch and 3/4-inch size jets, higher jet velocities were required with 1/4-inch and 3/8-inch diameter jets to provide ideal heat inputs for ignition.

TABLE 1. - Effect of jet and mixture velocity on the minimum hot gas ignition temperature of MIL-L-7808 engine oil with a 1/2-inch diameter hot air jet.
Fuel-air Weight Ratio - 0.55

Jet Velocity/ Mixture Velocity Ratio	36.5	52.1	52.5	52.7	54.7	81.0
Mixture Velocity, in/sec	1.0	0.7	1.0	1.3	1.5	1.0
Ignition Temperature, °F	1240	1255	1250	1270	1315	1300

Table 2 lists the minimum hot gas ignition temperatures obtained for the hydrocarbon fuel and engine oil vapor-air mixtures with the 1/4, 3/8, 1/2 and 3/4-inch diameter jets of hot air. These data are also shown graphically in figure 5 where the minimum ignition temperature values are plotted against the reciprocal of jet diameter (1/d); a similar plot including hot surface ignition temperatures is shown for the data found with n-decane vapor-air mixtures in figure 6, which is discussed later. As expected, the ignition temperatures of these combustibles decreased consistently as the heat source diameter was increased. However, for n-octane, the decrease was only 30° in varying the jet diameter from 1/2-inch to 3/4-inch. The use of larger size jets was not investigated because dilution effects could be great for the size of reaction chamber employed. For a given jet diameter, the ignition temperature values for the paraffin hydrocarbons increased only slightly with decreasing molecular weight. Also, the values for the JP-6 fuel tend to be the highest, and those for the MIL-L-7808 engine oil tend to be the lowest for jet diameters ≤ 0.5-inch. These results are unusual since the engine oil is a high AIT (~750° F) combustible, whereas the jet fuel is a low AIT (~450° F) combustible like the above paraffin hydrocarbons. However, the trend is consistent with that observed for these materials in autoignition and wire ignition temperature determinations with varying heat source diameters (2). Since the thermal stability of the combustibles at the pertinent temperatures may account for such observations, decomposition studies would be interesting to pursue, particularly with the adipate diesters which largely make up the engine oil.

TABLE 2. - Minimum hot gas ignition temperatures of the hydrocarbon fuels and engine oil (fuel vapor-air mixtures) with various hot air jets.
Mixture Flow Rate - 365 in³/min (N.T.P.)
Fuel-air Weight Ratio - Optimum for ignition (~ 0.5)

Diameter of Jet, inch	Jet Flow Rate, in ³ /min	Ignition Temperature, °F				
		n-Hexane	n-Octane	n-Decane	JP-6	Engine Oil MIL-L-7808
1/4	185	1630	1610	1600	1670	1530
3/8	185	1450	1440	1440	1500	1410
1/2	185	1280	1250	1220	1410	1250
3/4	365	1210	1220	1170	1290	1210

Comparison of Hot Gas and Hot Surface Ignition Temperatures

A comparison was made of the autoignition, wire ignition, and hot gas ignition temperatures of various paraffin hydrocarbon and JP-6 fuel vapor-air mixtures for cylindrical heat sources of about 0.4-inch diameter. Figure 7 shows the variation of these ignition temperatures with the number of carbon atoms present in each combustible; 12 carbon atoms were assumed for JP-6. The hot gas ignition data for the low molecular weight hydrocarbons are those of Vanpee and Wolfhard (6). They were obtained by injecting hot air jets at 365 in³/min, as compared to 185 in³/min for the data from the present study, into pure fuel under near stagnant conditions (~ 1 in/sec). According to the data in table 1, the difference in jet flow rates should not be serious. The autoignition temperatures (2) were determined in a quiescent air atmosphere by injecting liquid fuel into a heated cylindrical Pyrex vessel, 6 inches long. The wire ignition temperatures (2) were also obtained under near stagnant conditions (0.15 in/sec) where the combustible mixture was passed over a heated Inconel wire (2 inches long) mounted perpendicular to the axis of flow. Fuel-air weight ratio (0.3-0.5) and fuel residence time (> 1 second) were optimum for ignition for the data shown.

It is seen in figure 7 that the ignition temperatures generally decrease with increasing number of carbon atoms or molecular weight of the combustible, although all of the data are not consistent. In addition, the hot gas ignition temperatures are about 200° higher than the corresponding wire ignition temperatures and at least 300° higher than the AIT's. Somewhat the same behavior is found in comparing these ignition temperatures at various heat source diameters. Figure 6 shows such a comparison for n-decane vapor-air mixtures. Here, the hot gas ignition temperatures again are the highest, and their variation with the reciprocal of heat source diameter (1/d) resembles most closely that displayed by the autoignition temperatures; the wire ignition temperatures tend to display the least variation for 1/d values greater than 2-inch⁻¹. Such correlations may improve if the diameter as well as the length of the heat source are considered. The criterion of ignition is also important. For example, table 3 shows that luminous or "cool" flame reactions were observed at jet temperatures between 100° and 200° below those required for "hot" flame ignition. In the above correlations, the hot surface ignition temperatures referred to any visible flame whereas the hot gas ignition temperatures referred only to "hot" flame ignitions. Furthermore, the latter temperatures were measured near the jet base and were at least 200° higher than those at the plane where ignition occurred above the jet base (see table 3). Thus, the hot gas ignition temperatures of the given combustibles probably do not differ greatly from their hot surface ignition temperatures when the ignition criterion and the heat source dimensions are the same.

Considering that heterogeneous surface reactions are absent in hot gas ignitions, some variation probably exists between the hot gas and hot surface ignition temperatures of the given combustibles. At the same time, these hot gas ignition temperatures appear to vary somewhat the same as the autoignition or wire ignition temperatures with heat source diameter and with combustible concentration and composition. Even the anomalous hot gas ignition behavior displayed by the ethane and JP-6 fuels in figure 7 was also observed in the autoignition or wire ignition experiments. Apparently, the temperature dependency of the reactions controlling these hot gas and surface ignitions at atmospheric pressure did not vary greatly with the nature of the heat source.

Thermal Considerations of Hot Gas Ignition

Hot gas ignitions are unique in that the heat source is essentially free of surfaces and the pre-ignition reactions may be observed at relatively high temperatures and long duration (several seconds). Reaction kinetics involving hot gas ignitions of combustible mixtures may be studied by an analysis of rates of heat production within the hot jet (1,4,7). Such information should also be useful in the study of the heat requirements for the formation of "hot" and "cool" flames.

Thermal ignition of a combustible mixture by a hot gas jet should occur at a point in the jet stream where the heat generated by chemical reaction is greater than the heat lost from the system. If radial convection is assumed to be negligible and axial convection to be most important, the heat balance equation can be reduced to the following expression according to other investigators (1):

$$Q = \rho C_p v_y \left[\frac{\partial T}{\partial y} - \left(\frac{\partial T}{\partial y} \right)_{Q=0} \right] \quad (1)$$

where Q is rate of heat release by chemical reaction, ρ is density of the gas jet, C_p is specific heat, v_y is axial velocity, and T is jet temperature. Since $\rho C_p v_y$ varies slightly with temperature, the heat release can be determined by measuring the axial jet temperature profiles with combustible $\left(\frac{\partial T}{\partial y} \right)_{Q=0}$ and without combustible present $\left(\frac{\partial T}{\partial y} \right)_{Q=0}$. Such measurements were made here with the 1/2-inch diameter hot air jet flowing into preheated air or preheated fuel vapor-air mixtures at 350° F; a mixture temperature of 600° F was used with the MIL-L-7808 engine oil. The jet flow rate was 185 in³/min, the mixture flow rate was 365 in³/min, and the fuel-air weight ratio was about 0.25. Since the low jet flow rate produced steep axial temperature gradients, the use of equation (1) was only applicable to low jet heights. Furthermore, the Q values which were determined here should be considered only as relative values because of experimental uncertainties.

The above measurements were made in the center of the hot air jet where the radial temperature gradient was minimum. Figure 8 shows that the radial temperature profiles for the 1/2-inch diameter air jet ($T_{base} = 1265^\circ \text{ F}$) are reasonably symmetrical and are essentially flat up to a radial distance of about 0.05 inch for distances up to 2 inches above the jet base. In comparison, the corresponding axial temperature gradients are much greater because of the low jet flow rates employed here to obtain minimum ignition temperatures.

Figure 9 shows the axial temperature profiles obtained with preheated air and n-decane vapor-air mixtures at jet base temperatures of 1060° and 1265° F. At the lower temperature, heat evolution is not evident, and the curve describing the data with combustible present is below or coincides with the one found without combustible. Jet base temperatures in excess of 1060° F were required to form luminous reactions or "cool" flames. At 1265° F, the curve with combustible present is noticeably above the corresponding one without combustible at distances equal to and greater than 1-1/2 inches above the jet base. Here, a slight increase of jet temperature would be expected to overcome the thermal losses and produce "hot" flame ignition; a jet base temperature of about 1280° F produced ignition without the temperature probe present. Although sampling data of reaction products were incomplete, these data also indicated that the extent of reaction became noticeable at jet heights of about 1-1/2 inches for jet temperatures near critical for ignition. Similar axial temperature profiles were obtained with n-hexane, n-octane, JP-6 fuel, and MIL-L-7808 engine oil vapor-air

mixtures. In all cases, the temperature differences observed with and without combustible became significant at heights equal to or greater than about 1-1/2 inches above the jet base. Motion picture records of the ignition of n-octane vapor-air mixtures indicated that ignition of these mixtures occurs about 3 inches above the jet base with the 1/2-inch diameter jet at 1400° F (figure 10); the height at which ignition occurs can be expected to increase with decreasing temperature.

From the axial temperature profiles, the critical jet temperature and heat flux which may produce "hot" and "cool" flame reactions were determined for each of the combustibles. The reference temperature was taken at 1-1/2 inches above the jet base where initial reaction was noticeable; a higher level was avoided since the jet tended to be less coherent, in which case radial convection could be as important as axial convection. The gas velocity required in equation (1) was determined from photographs of dust particle tracks of dust entrained in the jet stream and illuminated at selected time intervals. A particle velocity of 73 in/sec was obtained near the center of the jet at distances between 1 and 2 inches above the jet base. In table 3, one observes significant differences between the temperatures which define the two ignition conditions for each combustible. However, the axial heat flux values ($A_{Q=0}$) vary little since the terms $\rho C_p v_y$ and T/y in equation (1) were not sensitive to moderate temperature changes. Thus temperature controls the hot gas ignitions to a greater extent than the rate of heat input; this behavior is not unusual for a heat source of relatively large diameter.

TABLE 3. - Critical temperature and heat flux for "cool" flame or luminous reactions and "hot" flame ignitions with 1/2-inch diameter hot air jet flowing into various combustible vapor-air mixtures.

Jet Flow Rate - 185 in³/min
 Mixture Flow Rate - 365 in³/min
 Fuel-air Weight Ratio - 0.25 to 0.30

Combustible	T _{base} °F	T ₁ ^{1/} °F	A _{Q=0} × 100 Btu/in ³ -sec	T _{base} °F	T ₂ ^{1/} °F	A _{Q=0} × 100 Btu/in ³ -sec	Q ₂ ^{2/} Btu/in ³ -sec
n-Hexane	1350	1100	5.55	1455	1190	5.60	1.25
n-Octane	1150	900	5.35	1330	1085	5.50	1.25
n-Decane	1060	750	5.30	1265	1065	5.50	2.15
JP-6 Fuel	1265	1035	5.45	1415	1195	5.55	2.45
MIL-L-7808							
Engine Oil	1320	1130	5.55	1415	1155	5.55	0.60

1/ Jet temperatures above which "cool" (T₁) and "hot" (T₂) flame ignitions can occur; measured at 1-1/2 inches above jet base.

2/ Heat release determined from axial convection with and without combustible ($A_{Q \neq 0} - A_{Q=0}$) at T₂.

The rates of heat release (Q₂) in table 3 correspond to temperature rises between 10° and 40° F which were observed at the jet height of 1-1/2 inches. If equation (1) is applicable, a temperature rise of about 160° to 180° F would be required to obtain a heat balance between the heat release rates and the axial convective heat losses (A) and thereby produce ignition. Indeed, temperature rises as high as about 140° have been observed in other similar experiments conducted at temperature conditions near optimum for ignition. Ordinarily, ignitions resulted before temperature rises of this magnitude were realized. Although such axial temperature measurements can be utilized to indicate the possibility of ignition, the use of equation (1) in this connection is more

applicable at relatively high jet flow rates which tend to produce uniform jets and small axial temperature gradients. Accordingly, similar data are presently being obtained at a jet flow rate of 365 in³/min to examine the reaction kinetics involved in the hot gas ignitions of the given combustibles.

CONCLUSIONS

The hot gas ignition temperatures of various hydrocarbon fuel and engine oil vapor-air mixtures decreased with increasing diameter of the hot air jet. These temperatures are not greatly dependent on fuel-air ratio and jet flow rate. They also do not differ greatly from hot surface ignition temperatures for comparable heat source diameters. The formation of "hot" flames and luminous reaction zones or "cool" flames in these hot gas ignitions appear to depend more on jet temperature than on rate of heat input.

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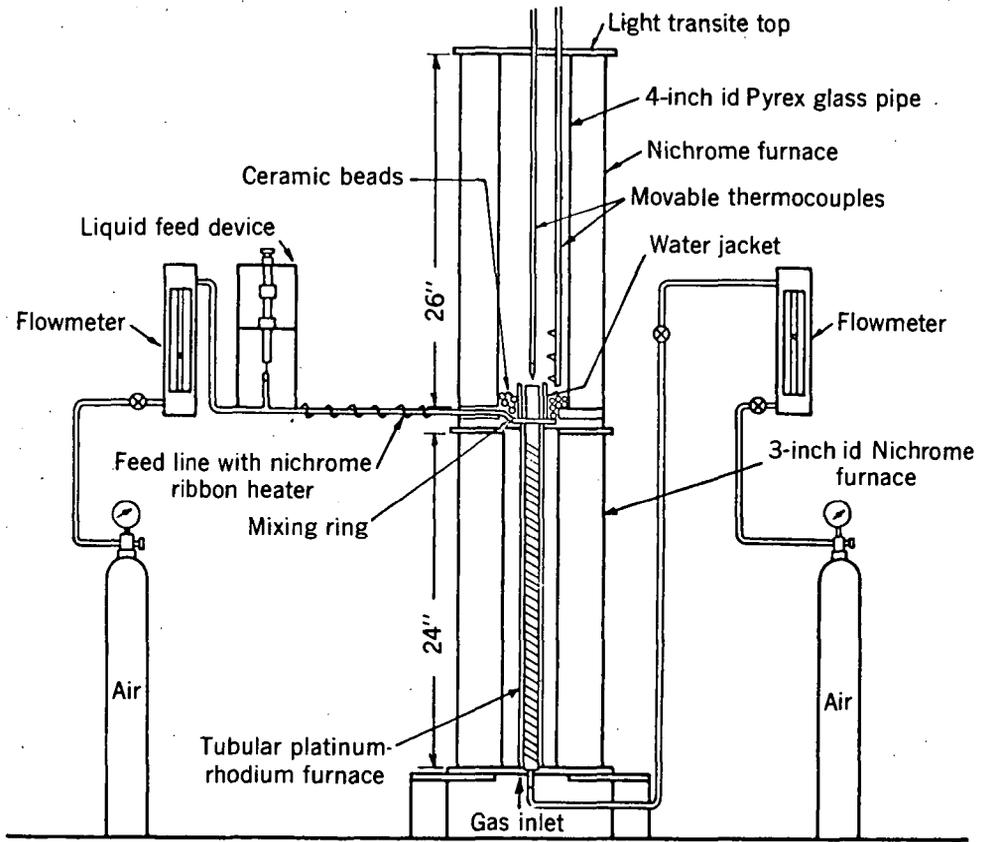


Figure 1. - Hot gas ignition temperature apparatus.

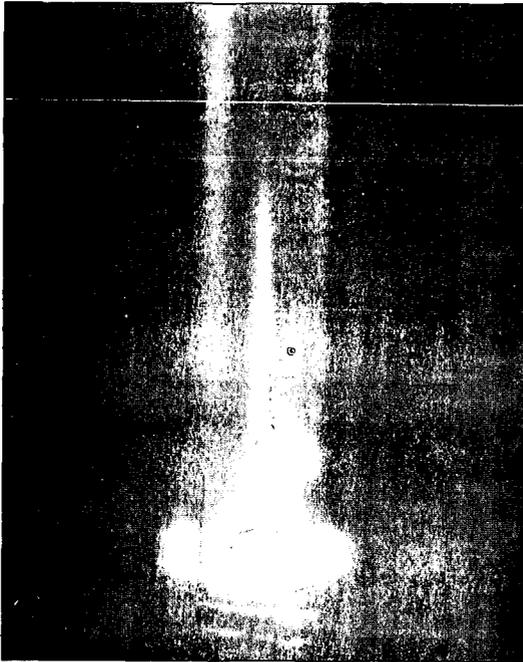


Figure 2. - Precursory flame formed in pre-ignition reaction of 1/4-inch diameter hot air jet (1670° F) with a uniform octane-vapor-air mixture at 350° F.
Jet flow rate - 185 in³/min Fuel-air weight ratio - 0.14
Mixture flow rate - 365 in³/min Scale: 1 inch = 0.935 inch

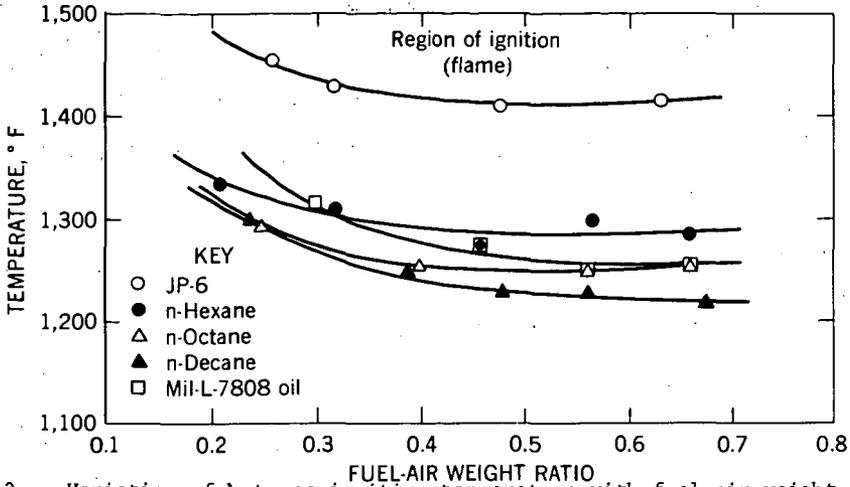


Figure 3. - Variation of hot gas ignition temperature with fuel-air weight ratio for various hydrocarbon combustible vapor-air mixtures with 1/2-inch diameter jets of hot air (Mixture flow rate - 365 in³/min).

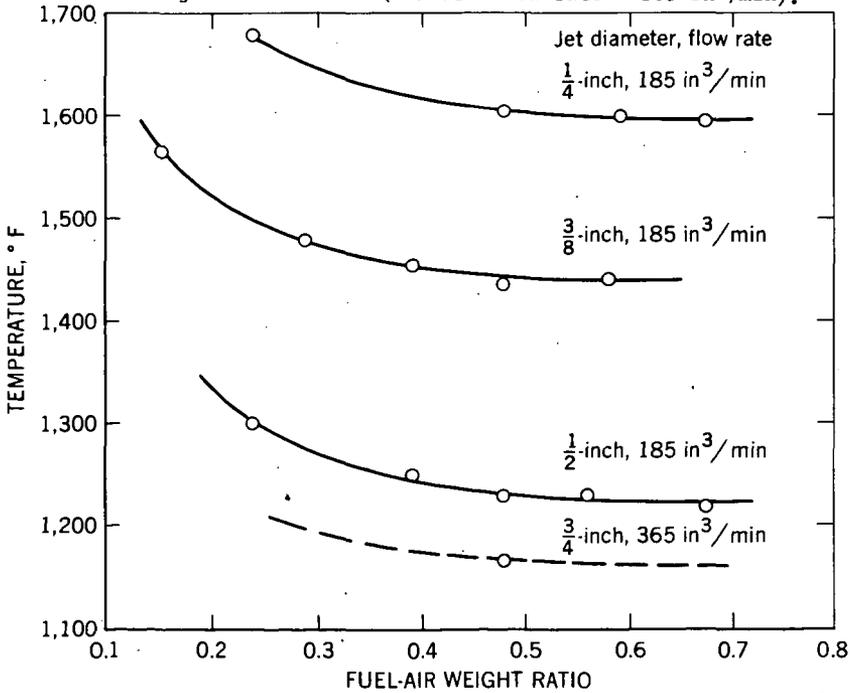


Figure 4. - Variation of hot gas ignition temperature with fuel-air weight ratio and diameter of hot air jet for n-decane vapor-air mixtures (Mixture flow rate 365 in³/min, N.T.P.)

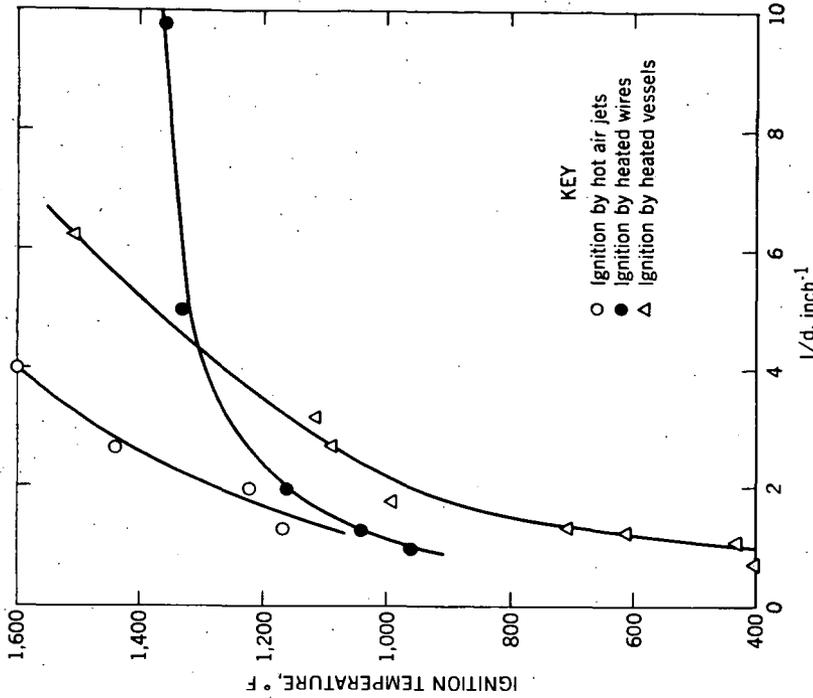


Figure 6. - Variation of hot gas and hot surface ignition temperatures with reciprocal diameter of heat source for n-decane vapor-air mixtures.

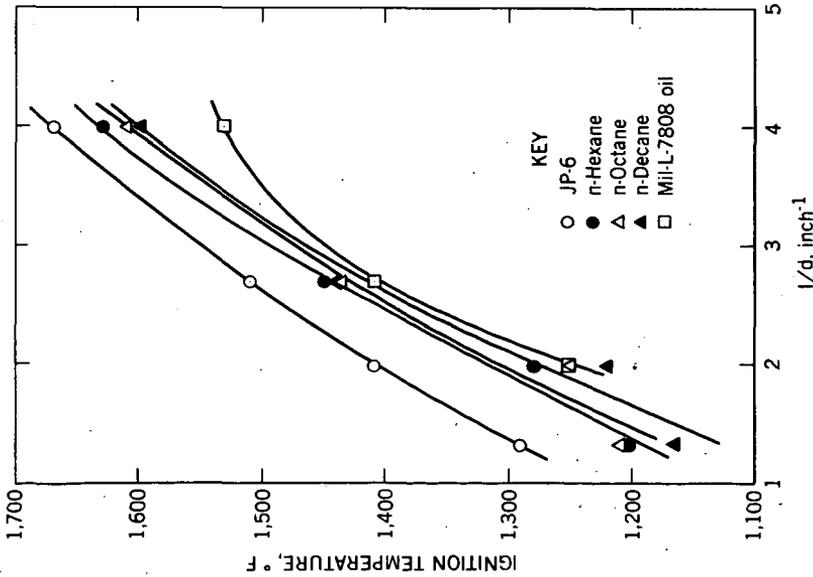


Figure 5. - Variation of hot gas ignition temperature with reciprocal diameter of hot air jet for various hydrocarbon combustible vapor-air mixtures (Flow conditions in figure 4 and table 2).

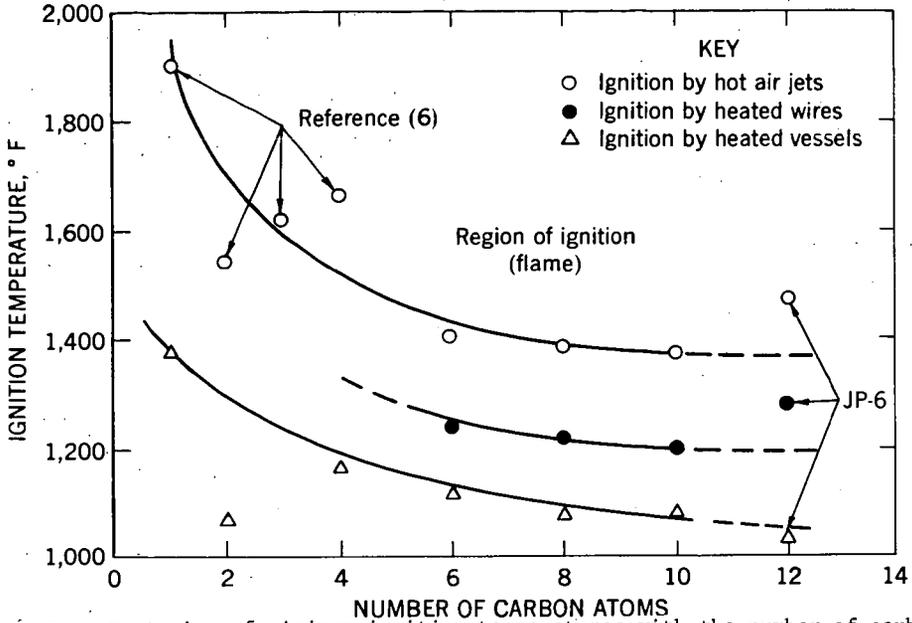


Figure 7. - Variation of minimum ignition temperatures with the number of carbon atoms for hydrocarbon (paraffin) and JP-6 vapor-air mixtures ignited with 0.4-inch diameter cylindrical heat sources.

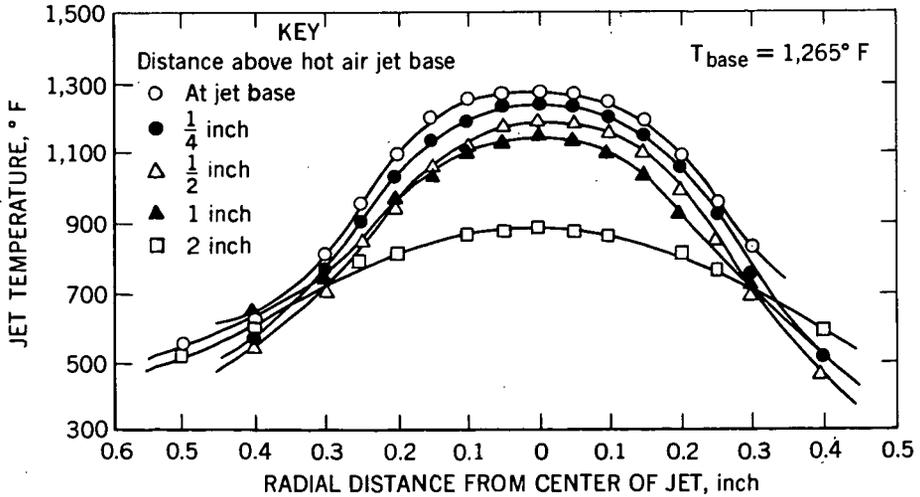


Figure 8. - Radial temperature profiles for 1/2-inch diameter jets of hot air flowing at $185 \text{ in}^3/\text{min}$, (N.T.P.) into preheated air at $350^{\circ}F$.

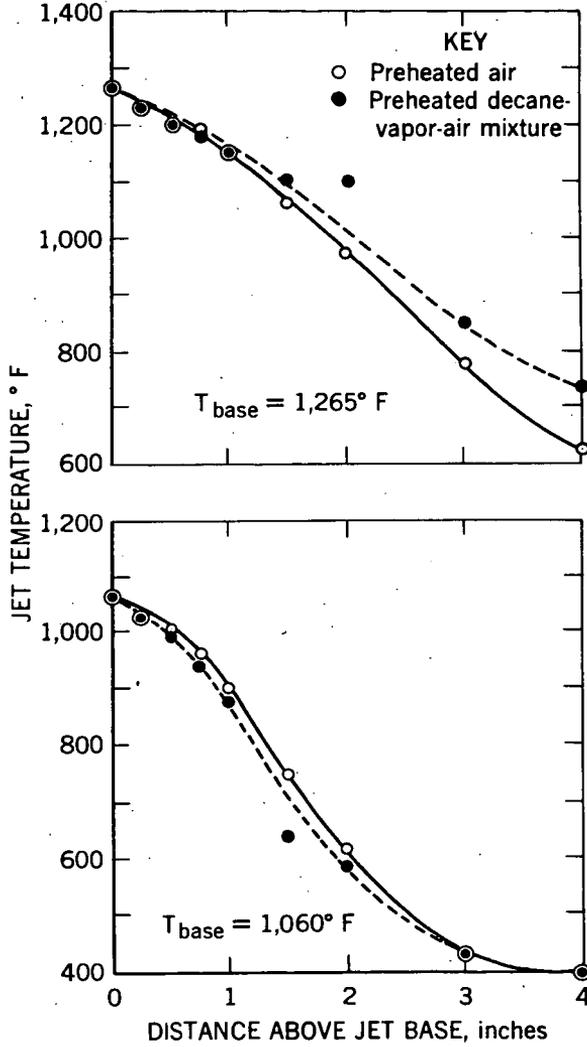


Figure 9. - Axial temperature profiles for 1/2-inch diameter jets of hot air flowing at 185 in /min, (N.T.P.) into preheated air and n-decane vapor-air mixtures at 350° F.

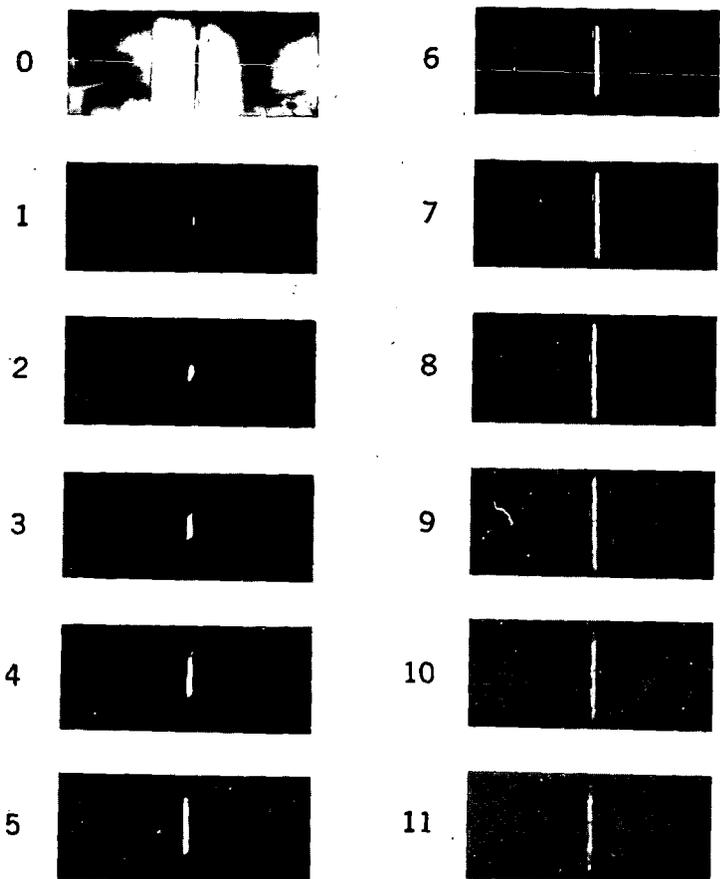


Figure 10. - Motion picture records showing the ignition of an n-octane vapor-air mixture with a 1/2-inch diameter hot air jet at 1400° F.

Jet flow rate - 185 in³/min (N.T.P.)

Mixture flow rate - 365 in³/min (N.T.P.)

Camera speed - 360 frames/sec

Scale: 1/4-inch = 5.4 inches for frames 1-11.

ELECTRICAL AUGMENTATION OF NATURAL GAS FLAMES

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I INTRODUCTION

Many industrial processes could make advantageous use of an economical source of heat at temperatures intermediate between those of combustion flames and those of electric arcs. This need has provided the incentive for numerous attempts to combine electrical energy with the heat released by combustion.

Combustion flames are, of course, limited in their heat release rate by reaction kinetics, and are limited in their ultimate temperature by the partial dissociation of the products of combustion.

The electric arc is not thus limited, but it has its own disadvantages. It is inherently a device characterized by extreme temperature gradients; that is, the electrically conducting path in the working fluid tends to contract into a very narrow, superheated channel, while the parallel surrounding paths carry little or no current and are relatively cold. The arc is further characterized by a relatively low voltage gradient along the conducting path; hence, it requires a high current if it is to dissipate substantial power in the gas. The high current, in turn, creates serious electrode maintenance problems, because the area of attachment of the arc at the electrodes is extremely small at any given instant. With a low voltage gradient through the gas, the energy dissipated as electrode losses (which are primarily a function of current density) is a relatively high proportion of the total energy input, thus tending to make the arc an inefficient means for heating the gas. In addition, the higher unit cost of electrical energy (versus combustion energy) puts the arc at an economic disadvantage.

Past research on electrical augmentation of flames, such as that of Southgate,¹ has utilized an electric arc in conjunction with the flame. Materials problems associated with the arc put a severe limitation on this technique, and interest in electrical augmentation of flames virtually disappeared until recently.

Renewed interest in the subject was initiated by a patent issued to Karlovitz² and by the preliminary development work on the patent concepts, by A. D. Little, Inc.^{3,4} This work demonstrated that large amounts of electrical energy could be imparted to a flame, in the form of a high-voltage, low-current discharge that was dispersed throughout the flame volume. Subsequently, several other publications^{5,6} have dealt with this subject. This paper will attempt to describe some of the performance characteristics obtained with the improved burner design.

II DISCUSSION OF THE DIFFUSE ELECTRICAL DISCHARGE

Gases at ordinary temperatures are very poor electrical conductors, because they have a very low concentration of free electrons and positive ions. As the temperature is raised, polyatomic gases tend to become more and more unstable and to dissociate into their constituent atoms. However, in most cases the constituent atoms are themselves highly resistant to further dissociation into ions and electrons. Only at extremely high temperatures (above 5000°K) do such elements as oxygen, nitrogen, hydrogen, and carbon begin to ionize to an extent sufficient to impart significant electrical conductivity to the gas.

In the region between 5000°K and 20,000°K, the extent of ionization of common gases is an extremely sensitive function of temperature, and the electrical conductivity rises by many orders of magnitude as the temperature rises. The gases are said to have a large "positive temperature coefficient of electrical conductivity."

Because of this large positive coefficient, an ordinary gaseous conductor is an inherently unstable resistive load, and cannot be placed directly across a constant-voltage source without degenerating into a virtual short circuit. (As the gas is heated by the electrical discharge passing through it, its conductivity rises almost without limit.) A "ballast," consisting of an appropriately large auxiliary resistance or inductance, must be placed in series with the usual gaseous conductor in order to achieve control of the current drawn by the latter. This is the usual method employed to stabilize an electric arc.

A large positive temperature coefficient of conductivity also results in a second effect within the gaseous conductor. The flow of current naturally takes the path of least resistance. If there are even minor local nonuniformities among various alternative paths, the most conducting path will be heated most rapidly and will therefore increase in conductivity most rapidly. Unless this process is somehow opposed, the flow of current will very rapidly contract into a single, very narrow channel.

Two main strategies are available to counteract filament formation. The first is to reduce the positive temperature coefficient of electrical conductivity of the gas to the minimum possible value. (If it could be reduced to zero, or made negative, no further strategy would be necessary.) The second is to reduce or eliminate random local nonuniformities in conductivity before they grow too large.

To implement the first strategy, the familiar tactic of "seeding" the flame is employed. Alkali metals (and their compounds) are much more easily ionized than are the constituents of the common gases. For example, as shown in Fig. 1, potassium chloride (added in low concentration to a flame) can approach complete ionization of the outer electron of the potassium atom at temperatures several thousand degrees Kelvin lower than those at which any significant ionization of the bulk flame gases occurs. Thus, the conductivity of such a seeded flame is provided almost entirely by the additive, and once the latter reaches a state of essentially complete ionization, the temperature coefficient of conductivity of the flame assumes a relatively low value. Only a few parts per million of "seed" material is required to furnish adequate conductivity for the flame to be able to dissipate a large amount of power at relatively modest voltages.

Implementation of the second strategy is possible in principle because the overheating of a conducting path (relative to its surroundings) and the contraction of that path into a narrow filament are both time-dependent phenomena; therefore, it should be possible to oppose them by means of the powerful mixing action that can be provided by turbulence. Such mixing would tend to level out any local nonuniformities in temperature and conductivity before they could develop too far.

A mathematical treatment of the condition required for prevention of filament formation has been described by Karlovitz.⁴ This treatment leads to the concept of a "critical voltage gradient," above which the rate of mixing provided by turbulence is inadequate to prevent the intensification of local inequalities in heating rate. Below the critical voltage gradient, the theory predicts that turbulence can act within a time interval comparable to that required for filament formation; this prediction has been verified experimentally. Thus, the two main tactics required for reduction of the diffuse discharge principle to practice are both available.

The initial mathematical model of Karlovitz is admittedly simplified, and will have to be refined to take into account such perturbing effects as dissociation of the working gas, nonequilibrium ionization (particularly during exothermic chemical reactions), and nonequilibrium electron capture (reported to be important during endothermic chemical reactions).⁷ Nevertheless, the simple theory has been found to provide a very useful guide for design.

III DESCRIPTION OF EXPERIMENTAL DEVICE

The work described here was conducted with a burner designed to operate on natural gas and air, at flow rates up to those corresponding to a maximum combustion heat release rate of 342,000 Btu per hour (equivalent to 100 kw of combustion energy).

The fuel and air were premixed and seeded with a dilute aerosol of potassium chloride. Combustion occurred in a constant-area duct and the diffuse electrical discharge was established in the fully combusted gases, immediately downstream of the combustion zone.

Figure 2 is a schematic representation of only the final stage of the device (in which the diffuse discharge takes place). This stage consists of a tube of refractory, electrically insulating material, bounded at both ends by metal electrodes. Provisions for cooling the tube and the electrodes are not shown in the diagram.

The electrodes are connected to a single-phase, 60-cycle power supply nominally designed for a power output of 100 kw, and actually capable of providing up to 150 kva at output voltages variable between about 2 and 8 kv. Inductive ballasting is provided, with the amount of inductance variable up to a maximum value sufficient to limit the short-circuit current to about twice rated current.

IV EXPERIMENTAL RESULTS

The initial burner configuration was similar to the original design described by Karlovitz, in that the discharge zone coincided with the combustion zone. Visually, the discharge did appear to be reasonably uniformly dispersed throughout the burner volume, and photographs taken with exposure times of the order of $1/50$ second, such as that in Fig. 3, confirmed this impression. However, when high-speed photographs were taken, such as that in Fig. 4, the discharge was shown to consist of one (or at most a few) rapidly wandering, contracted arc filaments. Regardless of the concentration of ionizing additive or the degree of approach stream turbulence employed, the contracted nature of the discharge persisted if more than 10% electrical augmentation was attempted.

At this point, the possibility had to be considered that the zone in which turbulent combustion was in process did not have the properties necessary to sustain a powerful diffuse discharge. Especially near the gas inlet end of the discharge tube, the ionizing additive could not be expected to be fully vaporized and uniformly dispersed, and severe local temperature and electrical conductivity gradients were likely to be present.

The nature of the discharge changed drastically when another section of the duct was added downstream of the combustion zone, and when the discharge was established in this final stage. Figure 5 is a frame from a high-speed movie (3000 frames per second), showing such a discharge at that point in a single half-cycle of a.c. corresponding to peak power. The average electrical power per cycle dissipated by the discharge during this movie was 100 kw, and the peak electrical power at the instant of the frame shown in Fig. 5 was over 200 kw, on the basis of simultaneous oscilloscopic records of discharge current and voltage. Stoichiometric proportions of natural gas and air were employed, at a total flow rate equivalent to 100 kw of combustion power.

The photograph shows that, under these conditions, no filamentary structure can be discerned in the discharge column. Other frames from the same film (such as that shown in Fig. 6) occasionally show a short length of arc filament immediately adjacent to the electrode (mainly next to the upstream electrode, during that half-cycle when it has negative polarity); however, this is not surprising, because the discharge generally anchors at a relatively small spot on the electrode, thus necessitating a very high current density in the relatively cool and nonconductive boundary layer surrounding the electrode. With proper preconditioning of the working gas, the main portion of the discharge column remains completely diffuse.

By permitting combustion to proceed to completion prior to the superposition of the electrical discharge, any undesirable nonequilibrium ionization due to exothermic chemical reactions during the

discharge is avoided. In fact, the combustion products have the desirable property of being able to undergo endothermic dissociation, thus providing a self-contained heat sink that should tend to help avoid localized overheating of the gas by the discharge. Another way of stating this is that the slope of the conductivity versus enthalpy curve is reduced by dissociation. This slope may be regarded as an even more direct criterion of the susceptibility of the gas to filament formation than is the slope of the conductivity versus temperature curve.

Further confirmatory evidence of the diffuse nature of the discharge in a well preconditioned gas is provided by oscilloscopic traces of current and voltage, such as those shown in Fig. 7. These may be contrasted with the traces shown in Fig. 8, obtained from a contracted arc superimposed on a seeded, turbulent, combusting gas stream, like that illustrated in Fig. 4. Several important differences between the two cases may be pointed out. First, during each half-cycle at a given average power level, the ratio of voltage to current (representing the instantaneous ohmic resistance of the discharge) fluctuates between much wider limits, and drops to much lower values at peak current, in the arcing case than in the diffuse case. Second, there is no pronounced rise in voltage during the extinction period in the case of the diffuse discharge. Third, the arcing case exhibits a rapid, high amplitude fluctuation in voltage that does not appear in the diffuse case. (In an inductively ballasted circuit, the current is prevented from undergoing rapid changes by the reactive back--emf developed across the inductance; therefore, any rapid fluctuations in discharge conductivity are exhibited as voltage fluctuations to a much greater degree than as current fluctuations.) An arc in a highly turbulent medium is stretched and distorted in a random fashion so that it would be expected to exhibit just the sort of random fluctuations in conductance as are observed. A diffuse discharge, on the other hand, has a cross-section that is large compared with the scale of turbulence, so that its average conductance is less easily perturbed by turbulent mixing.

One further observation may be cited in support of the conclusion that the discharge illustrated in Fig. 5 is truly diffuse. At a given power level, the total luminosity of the discharge region is remarkably low, compared to that of the arcing discharge. This low luminosity is consistent with the absence of superheated filaments. We have not quantitatively examined either the absolute intensity or the spectral distribution of the emitted radiation.

The theoretical enthalpy of the augmented stoichiometric, natural gas-air flame (referred to 298°K) is shown in Fig. 9, plotted against the augmentation ratio (the ratio of electrical power to nominal combustion power). The discharge has been successfully maintained in the

diffuse mode at average augmentation ratios up to, and even slightly in excess of unity, and at peak ratios more than twice as high as the average. At peak power in each half-cycle of a.c., the total enthalpy of the gas is so high that only the dissociation of the initial combustion products prevents the temperature from rising to a level at which the conductivity would rise excessively because of ionization of the bulk gas.

The theoretical equilibrium temperature and composition of a stoichiometric methane-air mixture are shown plotted versus total enthalpy, in Fig. 10. These data were obtained with the aid of a machine computation program developed in the course of this study, with the assistance of Dr. Stuart Brinkley of Combustion and Explosives Research, Inc. Experimental gas compositions for the effluent gases from the augmented burner indicate a close approach to equilibrium, after allowance is made for recombination reactions occurring in the sampling probe.

The experimentally determined rate of heat transfer from the augmented flame to a transient-type flux probe is shown in Fig. 11, as a function of total enthalpy and of distance from the burner exit plane. It may be seen that the over-all heat transfer coefficient is considerably higher than that typical of unaugmented flames, a result attributable to the effect of recombination reactions on the probe surface.

V SUMMARY

An improved version of an electrically augmented burner has been described in which a powerful, 60-cycle electrical discharge can be maintained in the combustion products from a natural gas-air flame, and in which the discharge can be maintained in a completely diffuse mode.

Proper preconditioning of the gas appears to be the most essential factor tending to oppose contraction of the discharge into an arc filament. A high degree of turbulence, both in the discharge zone and in the approach stream, also assists in combating filament formation, the effect being most noticeable at high electrical power levels.

The diffusely augmented flame has potential technical and economic advantages over other sources of high temperature heat, that are expected to be significant to chemical, metallurgical, and other industrial uses. Experimental work with respect to various such applications is continuing.

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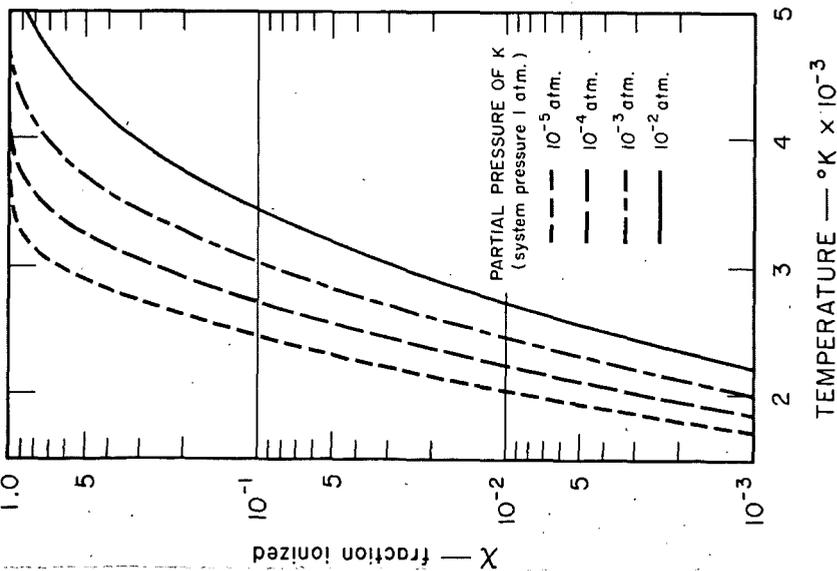


Fig. 1. -TEMPERATURE DEPENDENCE OF EXTENT OF IONIZATION

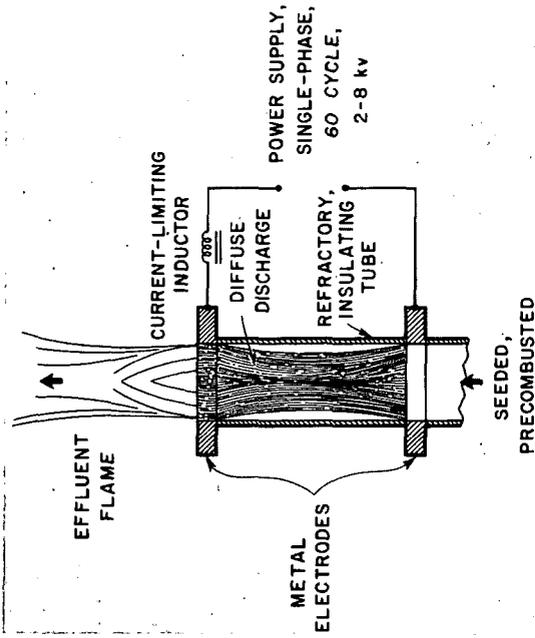


Fig. 2. -SCHEMATIC DIAGRAM OF FINAL STAGE OF ELECTRICALLY AUGMENTED BURNER

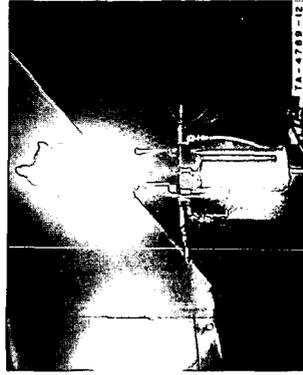


Fig. 3 -DIFFUSE APPEARANCE OF FILAMENTARY DISCHARGE AT SLOW SHUTTER SPEED

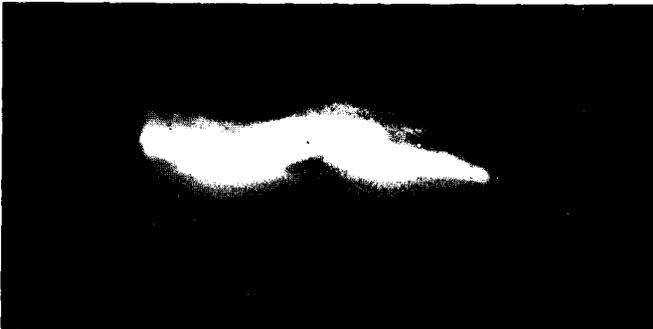


Fig. 4.-APPEARANCE OF
FILAMENTARY DISCHARGE
AT FAST SHUTTER SPEED

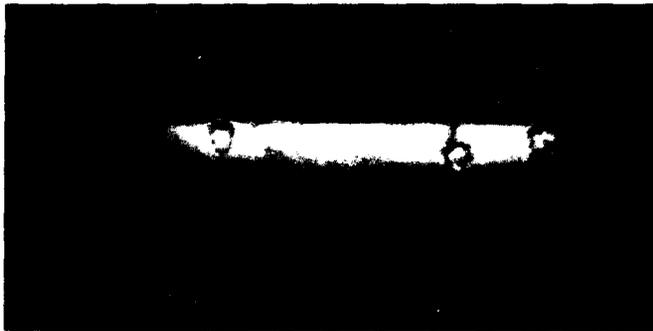
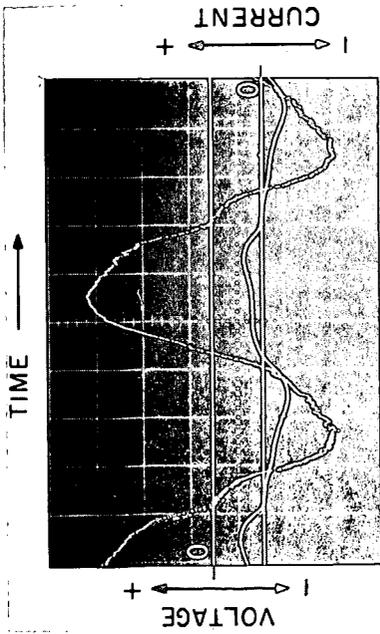


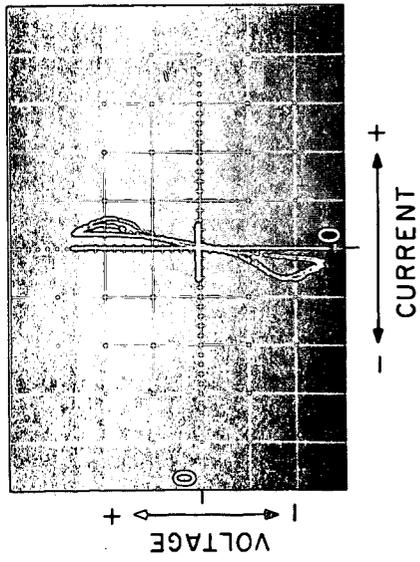
Fig. 5.-APPEARANCE OF
DIFFUSE DISCHARGE AT
FAST SHUTTER SPEED



Fig. 6.-MAXIMUM EXTENT
OF FILAMENT FORMATION
NORMALLY OBSERVED WITH
DIFFUSE DISCHARGE

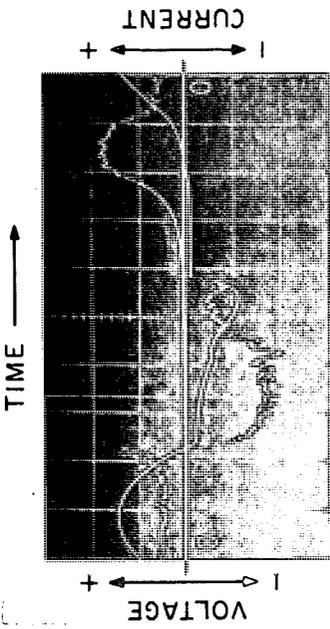


(a)

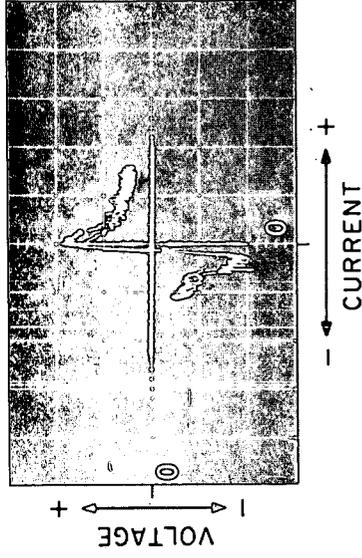


(b)

Fig. 7. -VOLT-AMPERE CHARACTERISTIC OF DIFFUSE DISCHARGE



(a)



(b)

Fig. 8. -VOLT-AMPERE CHARACTERISTIC OF FILAMENTARY DISCHARGE (at the same average power as that of Fig. 7)

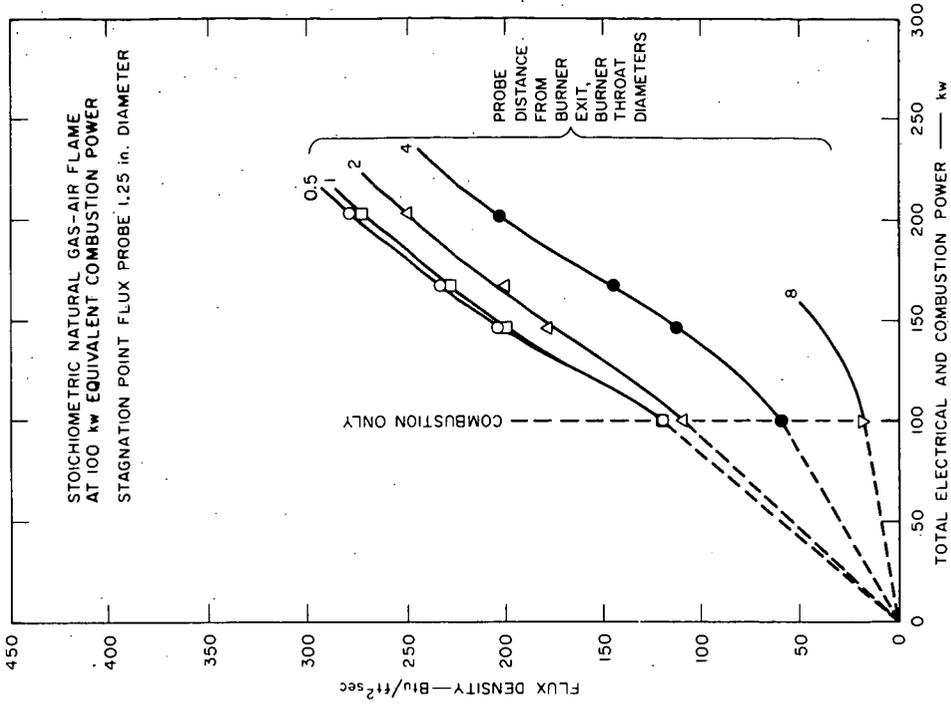


Fig. 11.—HEAT TRANSFER FROM ELECTRICALLY AUGMENTED BURNER TO A COLD-WALL, STAGNATION-POINT PROBE

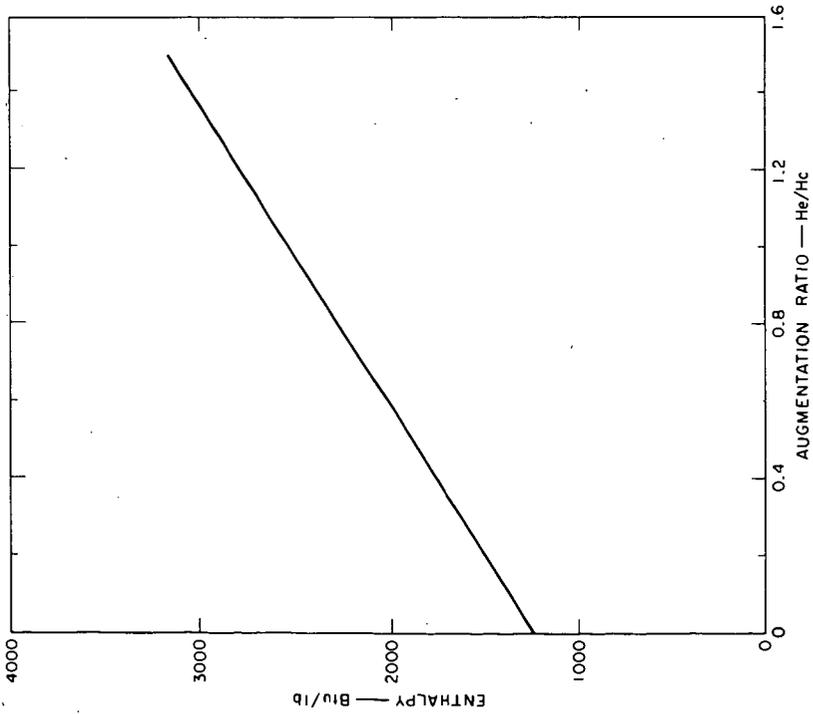


Fig. 9.—THEORETICAL ENTHALPY AS A FUNCTION OF ELECTRICAL AUGMENTATION RATIO

Figure to be distributed at meeting

Fig. 10.—THEORETICAL EQUILIBRIUM TEMPERATURE AND COMPOSITION AS A FUNCTION OF TOTAL ENTHALPY

MICROBIAL SYNTHESIS OF FOOD FROM COAL-DERIVED MATERIALS

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ABSTRACT

Recent reports on the microbial production of protein from petroleum fractions for use as human or animal food supplements prompted studies on the feasibility of producing microbial protein from coal-derived materials. Growth yields of four species of the yeast *Candida* on several low temperature lignite tar and Fischer-Tropsch synthetic liquid fuel fractions were compared with yields obtained on a normal paraffin fraction derived from petroleum. It was found just as feasible technically to produce microbial food material from low temperature tar and Fischer-Tropsch fractions as from petroleum-derived paraffins. Growth yields were as high as 99.8% (Fischer-Tropsch fraction), 95.2% and 84.2% (two low temperature lignite tar fractions) of the yields obtained on the petroleum-derived paraffin fraction. Similar studies on producing microbial food from coal acids, nitric acid-oxidized anthracite, and a mixture of polynuclear hydrocarbons found in relatively large amounts in high temperature coal tar revealed that these substrates did not support the growth of yeasts. However, a number of bacterial cultures grow at the expense of these materials. Determinations of growth yields are in progress.

INTRODUCTION

The problem of the world's population explosion is further compounded by an overall global food shortage. New or unusual sources of food, especially high quality protein, are needed as animal feed supplements or for human consumption. The Permanent Section on Food Microbiology and Hygiene, International Association of Microbiological Societies, in an unanimous resolution calling for an increased contribution of microbiology to world food supplies, outlined several research areas, including hydrocarbon microbiology, which might lead to increased world food production.^{1/} Recently, reports have appeared dealing with the microbial conversion of petroleum hydrocarbons to protein, vitamins or amino acids. High yields of yeast cells rich in protein and vitamins have been obtained at the expense of the n-alkanes (preferably C₁₀ or higher) in crude petroleum fractions,^{2-6/} feed stocks,^{7,8/} or with the pure hydrocarbons themselves.^{9-11/} Microbial synthesis of amino acids from petroleum products has also been reported.^{12,13/}

The rate of microbial protein synthesis far exceeds the rate at which animals synthesize protein. One 500 kg. cow fed by grazing can synthesize 0.5 kg. of protein per day,^{15/} whereas 500 kg. of microorganisms growing on paraffinic hydrocarbons could synthesize 1250 kg. of protein per day.^{3/} It has been estimated that 3 million tons of protein per year (equal to the world's present protein deficit) could be produced by microorganisms at the expense of only 1% of the world's annual production of 700 million tons of crude paraffinic petroleum.^{3/}

Coal, in addition to petroleum and natural gas, is one of the world's cheapest sources of fixed carbon and energy. The present paper reports the results of our studies on the feasibility of growing microorganisms for their food value at the expense of materials derived from coal.

EXPERIMENTAL

Materials. Three fractions of Bureau of Mines Fischer-Tropsch synthetic liquid fuel (iron catalyst) were used; fraction FTL (boiling range 0° to 204°), fraction FTD (boiling range 204° to 316°), and fraction FTW (boiling range > 316°).

Two fractions of hexane-soluble material from Rockdale lignite low temperature tar were obtained from the Texas Power and Light Company; the hexane solubles forerun (HSF) and the hexane solubles distillate (HSD). The HSF fraction constituted 7% and the HSD fraction 46% of the primary tar. The composition of fractions HSF and HSD are given in table 1. Phenolic compounds were removed by chromatographing fractions HSF and HSD on alumina with petroleum ether as the eluent to yield phenol-free fractions HSF \emptyset and HSD \emptyset . Approximately 20% by weight of starting material was removed by this procedure.

Table 1. Approximate composition of Rockdale lignite low temperature tar fractions, volume percent

Type of constituent	HSF	HSD
Caustic solubles	6-8	10-15
Acid solubles	2-4	1-3
Neutral oil	88-92	80-90
Paraffins	13-15	15-20
Olefins	40-55	40-50
Alpha-olefins	17-20	17-20
Aromatics	30-47	35-45

A paraffin-rich fraction (CTP) and a linear paraffin-olefin fraction (CTPO), both derived from the neutral oil of low temperature tar, were supplied by the Bureau of Mines' Morgantown Coal Research Center. Their analyses are given in table 2. The normal paraffin fraction derived from petroleum (PET) was a product of the Olefins Division of the Union Carbide Corporation. Our mass spectrometric analysis of this fraction is given in table 3.

Table 2. Analyses of paraffin-rich (CTP) and paraffin-olefin (CTPO) fractions from Rockdale lignite low temperature tar, weight percent

Carbon No.	CTP		CTPO	
	n-Paraffin	n-Olefin	n-Paraffin	n-Olefin
C ₈	0.2	--	--	--
C ₉	3.2	--	0.1	0.2
C ₁₀	11.7	0.7	1.3	1.6
C ₁₁	18.2	1.5	3.6	5.3
C ₁₂	22.4	3.3	5.8	7.6
C ₁₃	20.7	2.8	7.8	9.5
C ₁₄	10.8	3.7	7.5	10.9
C ₁₅	0.8	--	6.7	9.4
C ₁₆	--	--	4.6	5.6
C ₁₇	--	--	2.3	2.9
C ₁₈	--	--	4.2	3.1
	88.0	12.0	43.9	56.1

Table 3. Mass spectrometric analysis of n-paraffin fraction (FT) from petroleum

<u>Carbon No.</u>	<u>Volume percent</u>
C ₉	0.5
C ₁₀	7.2
C ₁₁	37.9
C ₁₂	29.1
C ₁₃	23.4
C ₁₄	1.9

Microorganisms. Cultures were obtained from soil by standard enrichment culture techniques or from the culture collections of the University of Pittsburgh, Syracuse University, and the University of Iowa.

Measurement of Growth Yields. Basal medium NX was prepared by adding NH_4NO_3 (5.0 g.), K_2HPO_4 (2.5 g.), and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (1.0 g.) to one liter of tap water. The pH was adjusted to 7.0 and any insoluble salts were removed by filtration. After sterilization by autoclaving, filter-sterilized yeast extract was added to a final concentration of 0.01%.

Inocula were prepared from cultures grown overnight in 50 ml. of Mycophil broth. The resultant growth was collected by centrifugation, washed twice in the sterile mineral salts solution of medium NX and resuspended in 20 ml. of the same solution. One ml. of washed cell suspension served as standard inoculum for all experiments.

For growth yield studies inocula prepared as above were added to 50 ml. of medium NX in 300-ml. Erlenmeyer flasks in triplicate. A quantity of substrate equivalent to 0.3 ml. was weighed into each flask. Triplicate controls consisted of inoculated flasks without added substrate. Cultures were incubated at 30° C. on a rotary shaker (225 r.p.m.) for six days. The resultant growth was collected on tared 2-inch diameter solvent resistant membrane filters (0.20 μ pore size), washed with 10-ml. volumes of acetone and n-hexane, dried overnight in air, and then weighed. All data are corrected for growth of controls.

RESULTS

More than 200 cultures of bacteria, yeasts, and fungi were screened for their ability to grow on Fischer-Tropsch and low temperature tar fractions. The yeasts *Candida lipolytica* strains 409, 409A, 409B, and *Candida tropicalis* strain 410 were selected as the most promising cultures with respect to total cell yield, ability to utilize diverse substrates, and resistance to reasonably high substrate concentrations. These preliminary studies also indicated that growth yields on Fischer-Tropsch fraction FTL and low temperature tar fractions HSF and HSF \emptyset were negligible. No further studies were made with these fractions.

Comparative Growth Studies. Pure Compounds vs. Coal-Derived Material. Absolute growth yields, in mg. dry weight per gram of substrate added, are given in table 4. The highest growth yields for all cultures (ranging from 433 to 719 mg. dry weight) were obtained with n-hexadecane as substrate; *C. lipolytica* 409 and 409A gave the best yields. Growth yields of 300 mg. or higher were obtained when 1-octadecene (*C. lipolytica* 409 and *C. tropicalis* 410) and Fischer-Tropsch fraction FTW (*C. lipolytica* 409B) served as growth substrates. Other substrates yielding

more than 200 mg. dry weight were paraffin-rich low temperature coal tar fraction CTP (all cultures), and Fischer-Tropsch fractions FTD (*C. lipolytica* 409B) and FTW (*C. lipolytica* 409). All cultures yielded less than 100 mg. dry weight on low temperature tar fraction HSDØ.

Table 4. Growth yields on pure compounds, low temperature tar, and Fischer-Tropsch fractions^{1/}

Substrate	<i>C. lipolytica</i>			<i>C. tropicalis</i>
	409	409A	409B	410
Low temperature tar				
HSDØ ^{2/}	83	43	0	62
CTP	272	276	294	208
Fischer-Tropsch				
FTD	134	115	280	-
FTW	287	127	344	200
Pure compounds				
1-Octadecene	357	295	244	344
n-Hexadecane	719	628	433	453

1/ Average of triplicate cultures. Data in mg. dry weight per gram substrate added, corrected for growth in controls.

2/ Phenols removed by two passes on alumina column.

Figures 1 and 2 illustrate comparative growth yields relative to n-hexadecane using the data in table 4. On all substrates tested, with the exception of low temperature tar fraction HSDØ, *C. lipolytica* 409B consistently gave yields greater than 50% relative to n-hexadecane and appears to be the most versatile culture. *C. tropicalis* 410 is noteworthy for its ability to utilize the terminal olefin 1-octadecene (75% relative to n-hexadecane).

Comparative Growth Studies. Petroleum-Derived Paraffin Fraction vs. Coal-Derived Material. Table 5 compares absolute growth yields on coal-derived material with yields on a normal paraffin fraction derived from petroleum (PET). The three *C. lipolytica* cultures yielded over 300 mg. dry weight on petroleum fraction PET. Yields greater than 300 mg. dry weight were also obtained on Fischer-Tropsch fraction FTW with *C. lipolytica* 409 and 409B. All cultures gave yields greater than 200 mg. dry weight on low temperature tar fraction CTP. *C. lipolytica* 409B and *C. tropicalis* 410 both produced more than 200 mg. of dry cells on low temperature tar fraction CTPO. *C. lipolytica* 409B also yielded more than 200 mg. dry weight on Fischer-Tropsch fraction FTD. All cultures yielded negligible or no growth on low temperature tar fraction HSD; however, upon removal of the phenolic constituents from this fraction, *C. lipolytica* 409B and *C. tropicalis* 410 produced more than 100 mg. of dry cell material.

Figures 3 and 4 illustrate comparative yields relative to petroleum fraction PET using the data in table 5. *C. lipolytica* 409 was outstanding on Fischer-Tropsch fraction FTW and low temperature tar fraction CTP, yielding 99.8% and 84.5%, respectively, of the growth obtained on PET. *C. lipolytica* 409A gave a relative growth yield of 70.5% on fraction CTP. The versatility of *C. lipolytica* 409B is again illustrated by relative yields ranging from 60.4% (fraction CTPO) to 85.3% (fraction FTW) on all substrates except fractions HSD and HSDØ. *C. tropicalis* 410 was outstanding in its relative ability to grow on low temperature tar fractions

CTP (95.2%) and CTPO (84.2%), although absolute yields were below those obtained with *C. lipolytica* 409B on the same substrates (see table 5). Also interesting is the apparent correlation between the abilities of *C. lipolytica* 409B and *C. tropicalis* 410 to use a terminal olefin (table 4) and their ability to grow on low temperature tar fraction CTPO which contains 56% of olefinic compounds (table 2). The *C. lipolytica* 409 and 409A cultures, which gave lower yields on 1-octadecene relative to n-hexadecane (figure 1), reflected this in their lower absolute and relative yields on CTPO compared with CTP (figure 3, table 5).

Table 5. Growth yields on low temperature tar, Fischer-Tropsch, and petroleum fractions^{1/}

Substrate	<i>C. lipolytica</i>			<i>C. tropicalis</i>
	409	409A	409B	410
Low temperature tar				
HSD ^{2/}	14	6	0	0
HSD ^{3/}	73	72	106	102
CTP	259	235	287	232
CTPO	113	124	233	205
Fischer-Tropsch				
FTD	114	150	243	0
FTW	306	167	329	161
Petroleum				
PET	307	333	385	244

1/ Average of triplicate cultures. Data in mg. dry weight per gram substrate added, corrected for growth in controls.

2/ Phenols not removed.

3/ Phenols removed by three passes on alumina column.

Growth Studies on Other Coal-Derived Materials. Studies were begun to investigate the feasibility of producing microbial food from other materials derived from coal, such as acids obtained by oxidizing coal with air, nitric acid-oxidized anthracite, and a mixture of polynuclear hydrocarbons found in high temperature coal tar.

A 56% aqueous solution of coal acids (obtained from the Dow Chemical Co.) and a water-soluble mixture of aromatic acids from the alkaline oxidation of coal (obtained from the Carnegie Institute of Technology) were tested as growth substrates for all of our yeast cultures. No growth was obtained. Similarly, soil enrichment culture procedures designed to favor the isolation of yeasts gave negative results. However, a number of bacterial cultures capable of growing on the coal acids were isolated; quantitative studies on growth yields are in progress.

A series of oxidation products from the nitric acid oxidation of anthracite was obtained from the Bureau of Mines Anthracite Research Center.^{14/} The acid-soluble residue of the 1000-hour oxidation time supports the growth of a bacterial culture previously isolated on one of the coal acids. Growth yield studies and enrichment culture procedures are in progress.

A mixture of polynuclear hydrocarbons found in relatively large amounts in high temperature coal tar was prepared. It was composed of (by weight percent) 1-methylnaphthalene, 59.2; 2-methylnaphthalene, 16.3; naphthalene, 11.9; phenanthrene, 12.5. A number of bacterial cultures, but no yeasts, capable of growing on this material have been isolated from soil. Growth yield studies are in progress.

DISCUSSION

In practice, over 80% conversion of hydrocarbon substrates to cell material has been obtained.^{3,6,9-11/} Although our absolute growth yields on pure hydrocarbons, petroleum, Fischer-Tropsch, and low temperature tar fractions were somewhat lower, it must be remembered that our experiments were designed solely to test the feasibility of using these substrates for microbial food production. Improvements in the nutritional quality of the growth medium, closer control of pH, more efficient aeration, and other practices of the fermentation microbiologist's art will undoubtedly result in higher cell yields.

It is clear that some of the substrates derived from coal which were tested are closely comparable to petroleum-derived normal paraffins in their ability to support microbial growth with the concomitant production of cell material (food). Paraffin-rich low temperature tar fraction CTP and Fischer-Tropsch fraction FTW were outstanding in this regard.

Oxidized coals and polynuclear aromatic hydrocarbons may be suitable for the growth of bacteria, rather than yeasts, for use as food material. Further experiments along this line are in progress.

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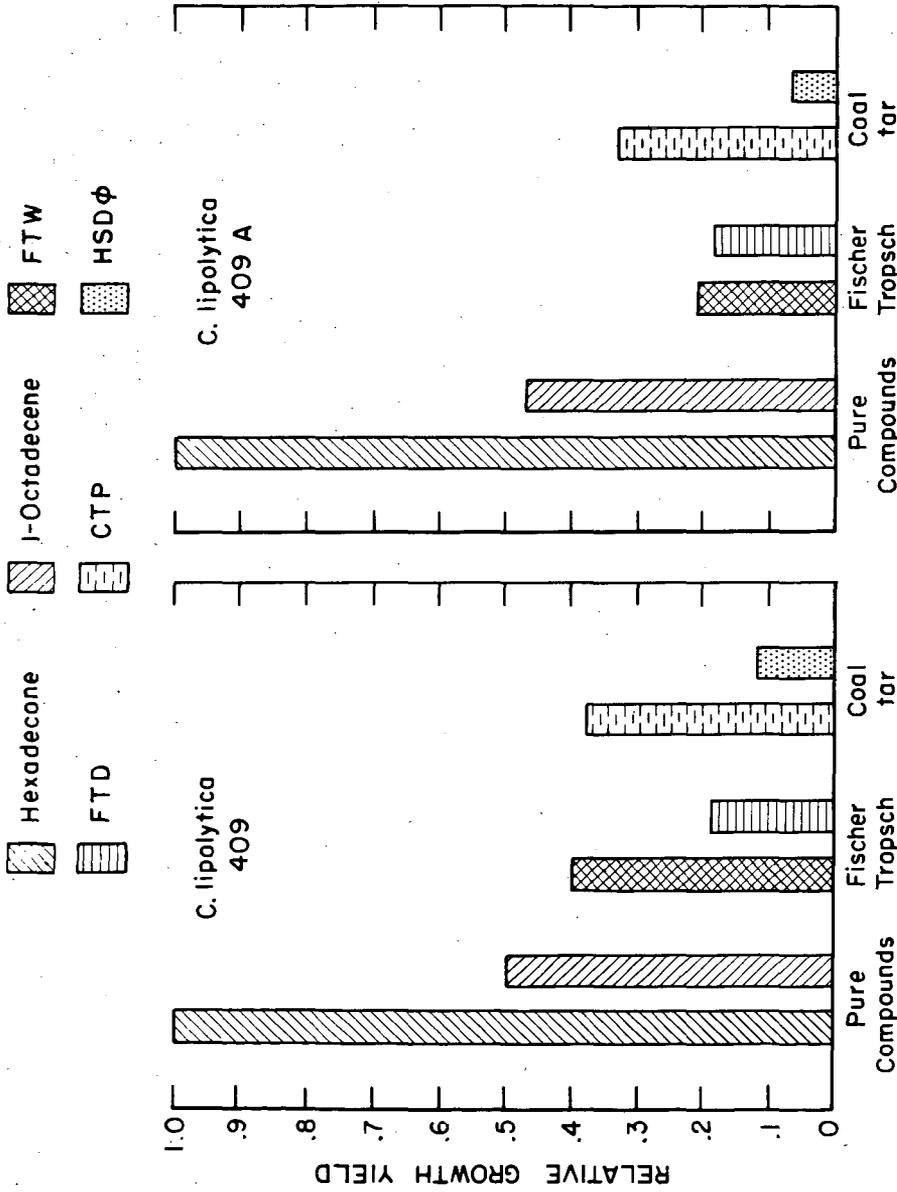


Figure 1.- Growth yields relative to n-hexadecane.

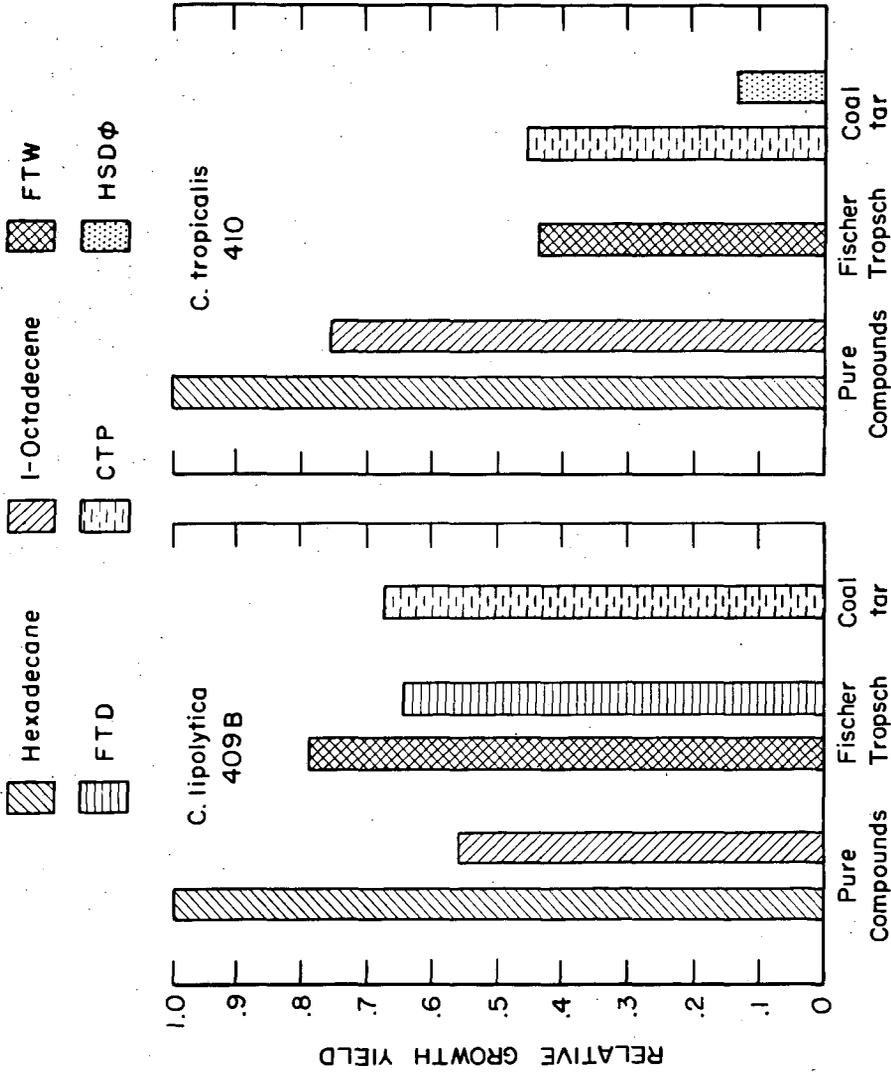


Figure 2.-Growth yields relative to n-hexadecane.

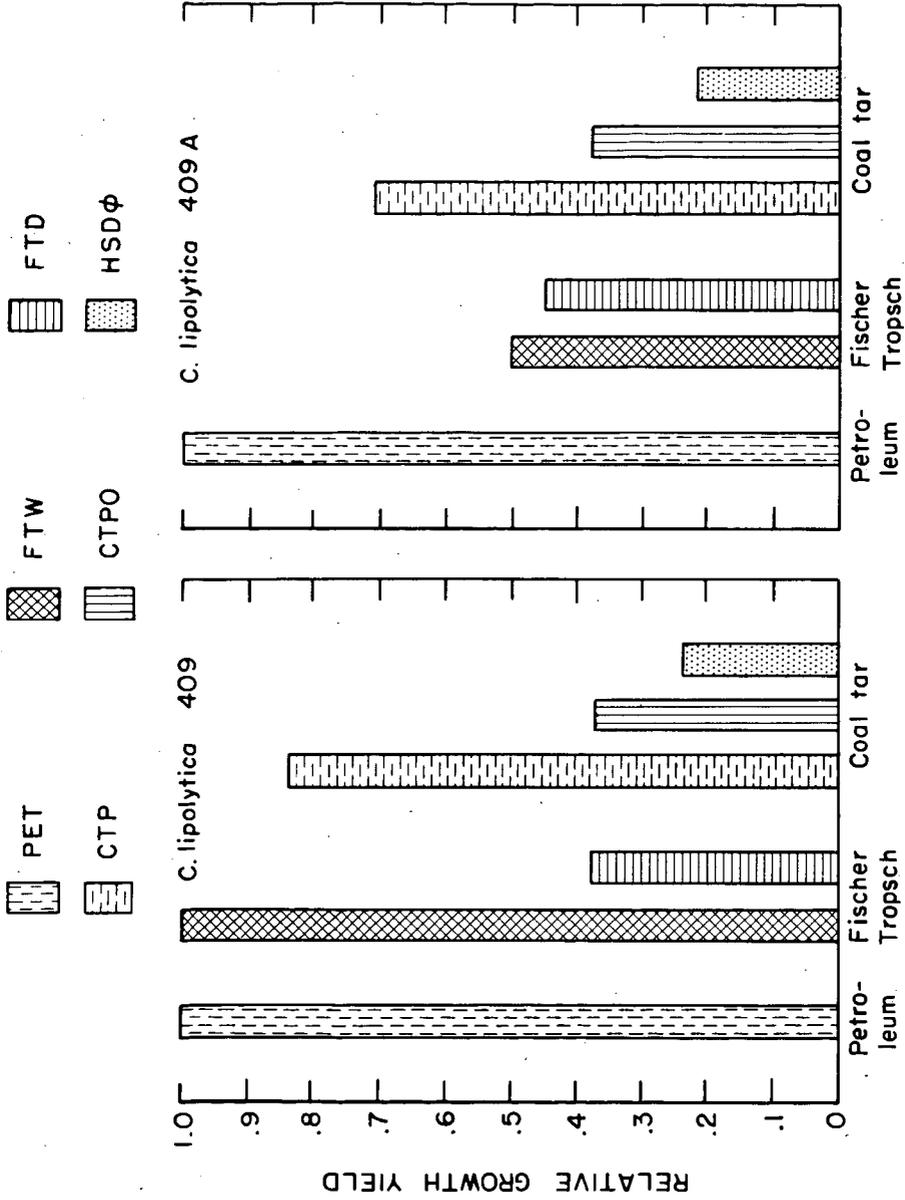


Figure 3.- Growth yields relative to petroleum.

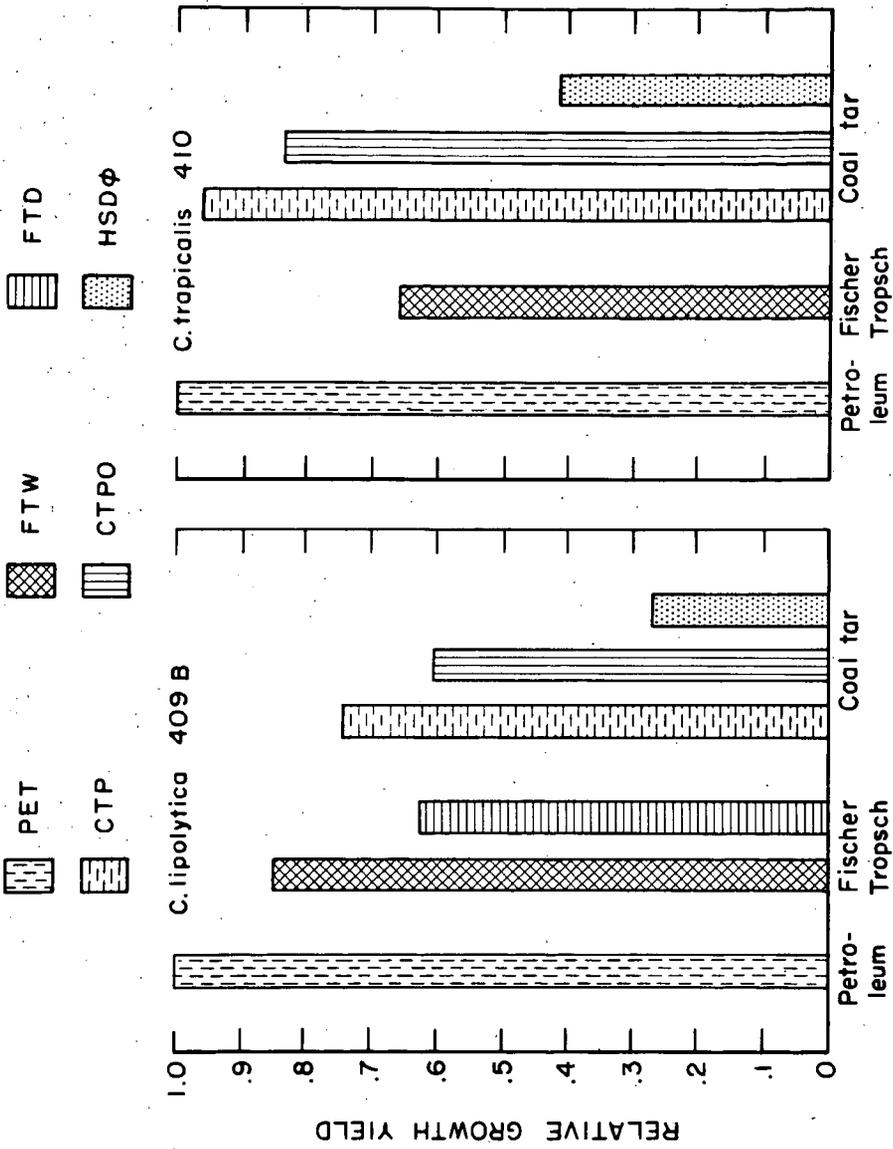


Figure 4.-Growth yields relative to petroleum.

The Effect of Air Oxidation on the Caking Properties of
Pittsburgh-Seam Coal

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INTRODUCTION

Production of synthetic liquid and gas fuels is a potential means for increasing the market for coal. The demand for fuel is high in the East and Midwest, but unfortunately most coals in these sections become sticky and agglomerate or cake when they are heated through the range of 300°-400° C. If they could be made noncaking, they would be suitable for fluidized-bed gasification, hydrogenation, and carbonization.

Nathan^{7/} destroyed the caking property of coal (10 to 400 mesh) by pre-treating it in air at 316°-441° C. Channabasappa^{1/} treated coal of 88 to 98 percent through 100 mesh with air as well as other gases at a temperature range of 200°-382° C. Schmidt^{8/} decaked Pittsburgh-seam coal of 0 to 1/4-inch size with air at 99.3° C. He also noted that the agglutinating value of the coals decreased as the oxidation of the coals increased. Minet^{6/} oxidized coal with steam plus air at 370°-430° C in the first stage of a carbonization process, and Williams^{9/} treated coal (80 percent through 1/8 inch screen) with an oxygen-containing gas at 80°-300° C.

Pittsburgh-seam coal is highly caking. In earlier work at the Bureau^{2/} it was made nonagglomerating, and with only slight variation the treatment was successfully applied to other caking coals. In this previous work the caking property of Pittsburgh-seam coal was destroyed by treating it in both static^{4/} and fluidized^{2,3/} beds with steam plus oxygen or air. To extend this study the present program was to treat Pittsburgh-seam coal with air only, to study the effect of operating variables such as mesh size, temperature, residence time and pressure, and to deduce the changes that may take place in the coal during treatment by carbonizing the treated coal.

Decaking was considered successful if the free-swelling index (FSI) of the treated coal (char) did not exceed 1-1/2 and the treated coal did not agglomerate when it was heated in a hydrogen atmosphere to 900° C.

STATIC-BED EXPERIMENTATION AND RESULTS

In the static-bed experiments fine particles of Pittsburgh-seam coal were spread in 100 x 50 ml dishes to a 1/2-inch depth, placed in a large drying oven, and heated in air to 95°-100° C. To decake these coals, using an FSI of 1-1/2 or less as indicating satisfactory decaking, required about 16 hours treatment under these conditions for 150-200 mesh^{a/} coal, 24 hours for 100-150 mesh, and 50 hours for 48-100 mesh (figure 1). At the end of 64 hours the 18-48 mesh coal had an FSI of 3-1/2. The oxygen content of all coals increased with time; with the finer coals the increase was more rapid. The loss in volatile matter averaged about 3 percentage points (a change from 40 percent volatile matter in the raw to 37 percent in the treated coal). About 6 months after the original data were collected, additional tests were made on different batches of coal of 18-48 and 48-100 mesh sizes. These results are shown on figure 1 as larger squares and dots. While the later data with the 18-48 mesh coals correlate with the earlier results, data from the 48-100 mesh size show some discrepancies. These results, although not exact due to the method of operation, demonstrate that treating fine coal in air at 100° C will decake the coal, but at least 16 hours time will be needed. These tests also indicate that it is not safe to assume that there is no change in the properties of fine coal dried in air at this temperature.

FLUIDIZED-BED EXPERIMENTATION AND RESULTS

Apparatus for the fluid-bed experiments is shown in figure 2. The reactor is a stainless steel tube of 1-inch diameter with an expanded section of 2-inch diameter at the top. The 29-inch section containing the fluidized bed of coal is heated electrically. Thermocouples are inserted inside a well placed down through the center of the reactor. Raw coal from the continuous feeder is entrained in the air stream and carried into the bottom of the reactor. The oxygen in the air renders the coal noncaking at specified temperatures, and the treated coal overflows into a collection vessel. Gases, tars, and dusts are discharged from the top of the reactor.

Because the height of the fluidized bed is constant, the rate that the coal is fed determines the residence time of the coal in the reactor. Only 40 minutes were required to decake Pittsburgh-seam coal in the fluid bed at 200° C for the 150-200 mesh size and 400° C for the 18-48 and 48-100 mesh size (figure 3). The results are more relative than absolute, but the trends are realistic. The oxygen content of the coals reached a maximum between 300° and 400° C and was less at the higher temperatures. The

^{a/} All mesh sizes are Tyler Standard Screen Series.

temperature at which it reached a maximum depended on the mesh size. As the temperature was raised to 300° C, the volatile-matter content decreased gradually, and then precipitously at higher temperatures. The minimum loss in volatile matter was about 3 percentage points at 300° C.

With the same 40-minute residence time the 150-200 mesh coal was treated at pressures of 1, 2, 5, and 10 atmospheres and 100° to 450° C (figure 4). At atmospheric pressure the coal became noncaking at 200° C; at 5 atmospheres it became noncaking at about 175° C, and at 10 atmospheres the coal burned above 150° C. At 150° C there was little change in the FSI. The oxygen content increased at higher pressures, the maximum being about 13 percent at 2 atmospheres and 300° C.

The volatile matter decreased at higher temperatures, but the change in volatile matter was insignificant at higher pressures. The least volatile matter was removed (3 percentage points) when the coal was treated at 200° C and atmospheric pressure.

Shortening the residence time to 20 minutes had little effect on the volatile matter and the FSI of the treated coal (figure 5) when compared with 40 minutes (figure 4). The amount of oxygen absorbed was the same as in the previous test at 2 atmospheres and 300° C. As the same results were obtained with the shorter residence times, the controlling variable seems to be temperature. Residence time might be shortened even more, but the limit of operability had been reached and the coal feed could not be increased to make such a test.

Also at the 20-minute residence time it was possible to continue the treatment at 5 atmospheres to 400° C, whereas at the 40-minute residence time the coal burned uncontrollably above 200° C. Thus the maximum oxygen content of the coal became 17 percent. Why coal could be treated at higher temperature with shorter residence time is not clear.

These curves show that the FSI is substantially independent of pressure, but highly dependent on coal size. More oxygen is absorbed by the coal at higher pressures and no more volatile matter is lost. The decrease in volatile matter is primarily a function of temperature, at least in the pressure range up to 10 atmospheres. Of course, when the pressure is increased, the air flow must also be increased to maintain fluidization; however, the oxygen/coal ratio at the different pressures indicates that pressure has more effect than air flow.

When the tests were made at 5 atmospheres, two samples of treated coal were taken at each temperature. One sample was evacuated to 30 mm absolute pressure to determine if oxygen taken up during treatment could be removed. Comparison with the nonevacuated sample showed that it could not. Consequently the additional oxygen must have chemically reacted in the coal to form a coal-oxygen complex.

CARBONIZATION TESTS: EXPERIMENTATION AND RESULTS

Comparing the results of low-temperature carbonization of coal fluidized in air at 230° C with raw coal gives a clue as to what changes take place in the volatile matter during the air treatment (table 1). The carbonization unit has a charging vessel at the top (figure 6)². After the reactor reached the desired temperature, the valve below the charging vessel was opened to allow the coal to drop into the heated zone.

TABLE 1.- Batch carbonization tests at 538° C (1,000° F) and 427° C (800° F) at 30-minute residence time

Type of coal	Raw	Treated ^{1/}	
Temperature, °C	538	538	427
Gas analysis, vol-pct			
H ₂	13	10	2
N ₂	0	0	1
CO	6	16	19
CH ₄	53	39	17
C ₂ +	22	13	9
CO ₂	6	22	52
HV	1060	750	410
Cubic feet tail gas per ton feed coal	1100	1600	400
Solids feed analysis, wt-pct, MAF			
Volatile matter	40.2	35.6	36.4
Fixed carbon	59.8	64.4	63.6
Hydrogen	5.6	4.8	4.9
Carbon	83.6	80.1	80.3
Nitrogen	2.3	2.2	1.6
Oxygen	6.6	11.1	11.2
Sulfur	1.9	1.8	2.0

^{1/} Made by fluidizing coal in air at 230° C for 30 minutes.

Proximate analysis (table 1) shows that treated and raw coals differ mainly in their volatile matter and oxygen content, the treated coal containing the more oxygen. The higher the oxygen content in the feed, the more carbon oxides in the gas produced by carbonization at 538°--12 percent for raw and 38 percent for treated coal. The heating value of the gas decreased as the carbon oxide yield increased, dropping from 1,060 to 750 Btu per cubic foot.⁵ This observation⁸ on carbon oxides is in agreement with the data of Juntgen⁷ and of Schmidt⁸.

The quality of the volatile matter differs for raw and treated coal. The treated coal carbonized at 427° C yielded primarily carbon oxides (table 1), indicating that the additional oxygenated compounds in the treated coals are reacted faster than the volatile matter in the raw coal. At 538° C the percentage of carbon oxides is less because after the supply of oxygenated compounds is depleted, the usual pyrolytic reactions predominate.

Table 1 gives the volatile matter of the raw coal as 40.2 percent and that of the treated coal as 35.6 percent. The larger quantities of carbon oxides given off during carbonization of the treated coal indicate that its volatile matter has been supplemented by the oxygenated compounds formed during treatment.

CONCLUSION

Tests show that Pittsburgh-seam coal, a highly caking coal, can be made nonagglomerating by heating in air in a static bed at 100° C for about 16 hours (150-200 mesh) or 50 hours (48-100 mesh).

In a fluid-bed reactor the finer mesh coal (150-200 mesh) can be made noncaking in 40 minutes by treating and fluidizing it with air at 200° C. As the temperature is increased, more oxygen combines with the coal until at about 350° C (depending on the coal size) the burning of the coal becomes uncontrollable. The percentage of oxygen in the coal increased from about 8 percent in the raw coal to as high as 17 percent when the coal was treated at 5 atmospheres pressure. Satisfactory decaking (as indicated by an FSI of 1-1/2 or less) was obtained with a volatile loss of 3 percentage points (10 percent of the volatile matter).

Carbonization tests indicate by the greatly increased yield of carbon oxides from the treated over the raw coal that a large amount of oxygenated compounds is included in the volatile matter of the treated coal. These additional compounds had to come from the treatment.

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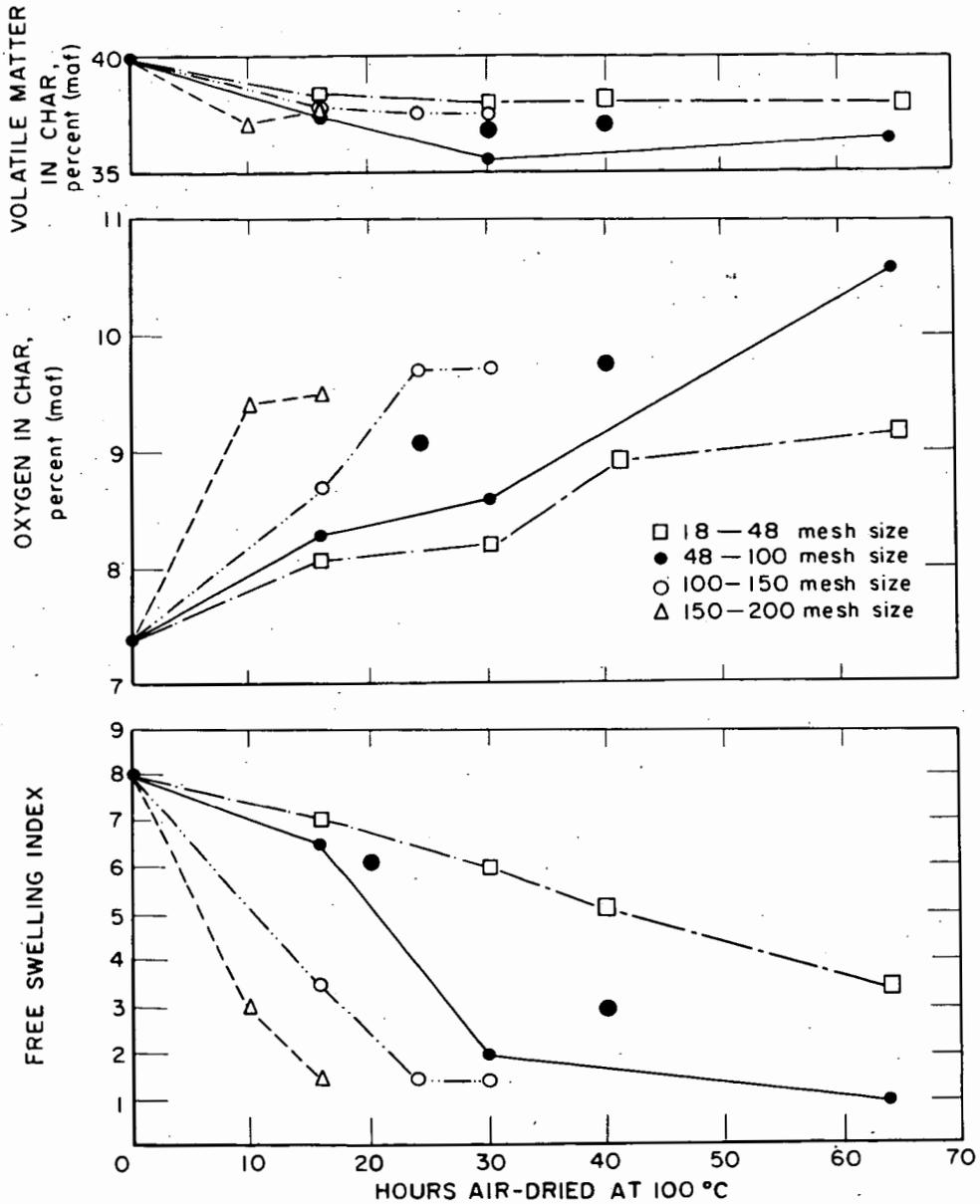


Fig. 1.-EFFECT OF RESIDENCE TIME ON THE FSI, VOLATILE MATTER, AND OXYGEN CONTENT OF CHAR OF PITTSBURGH-SEAM COAL TREATED IN AIR AT 100°C IN A STATIC BED

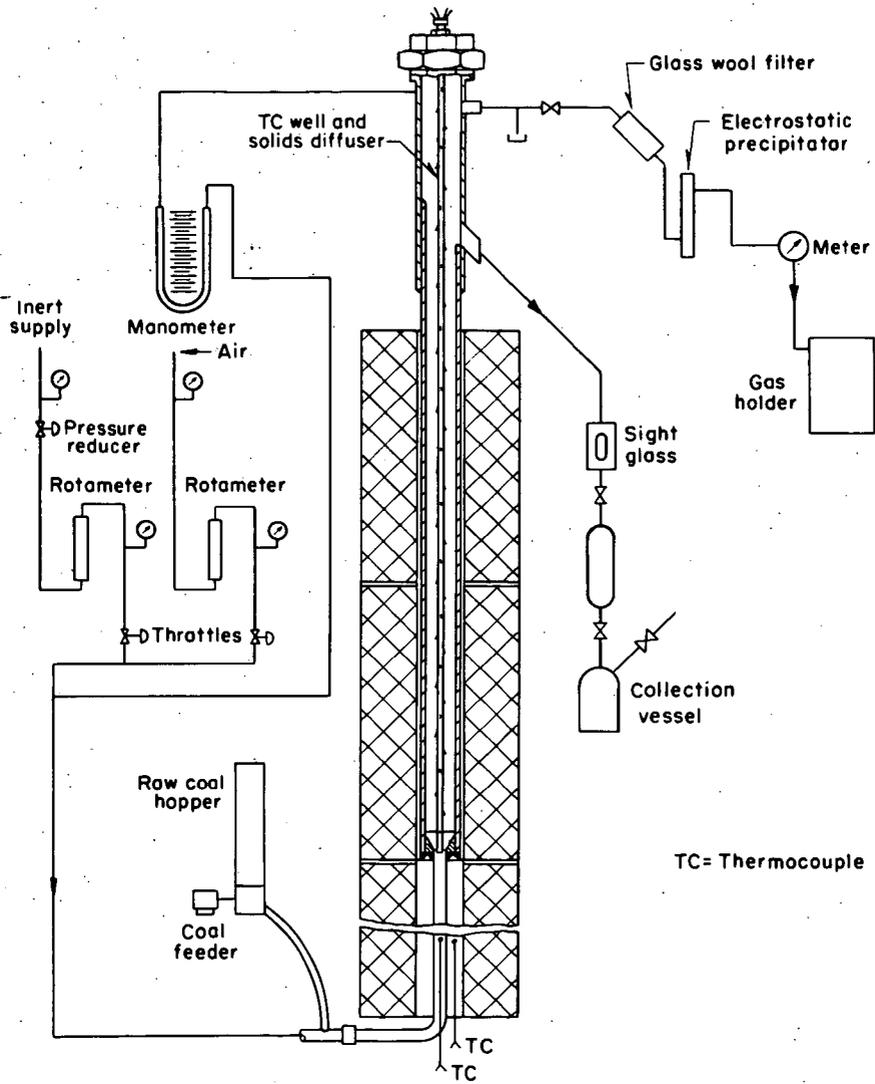


Fig. 2.-CONTINUOUS FLUIDIZED-BED COAL PRETREATER

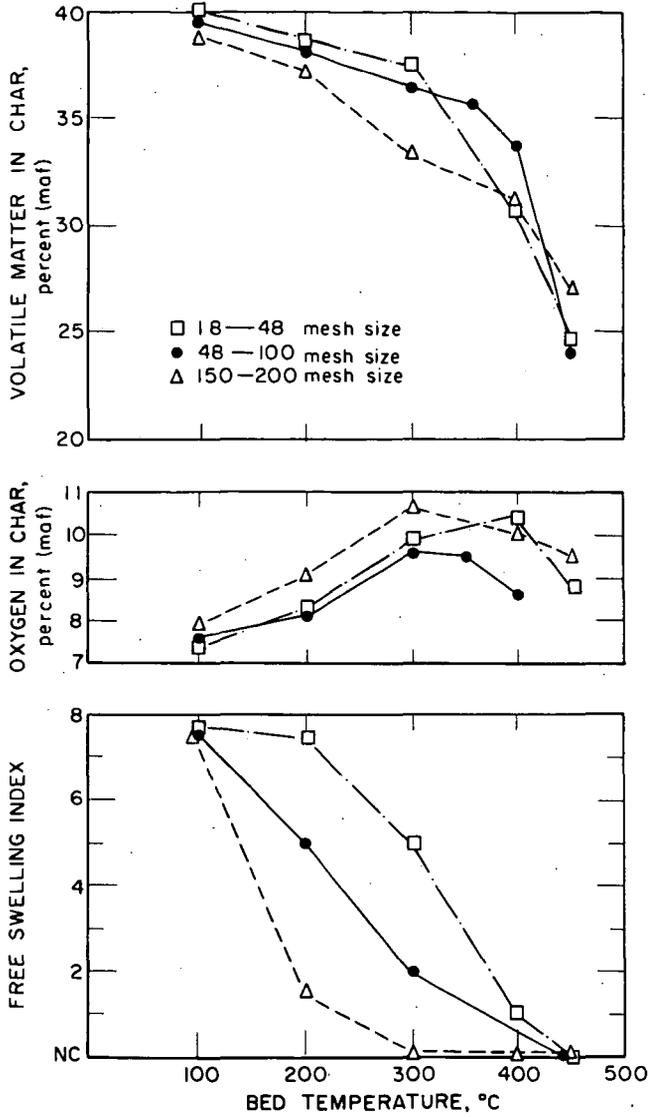


Fig. 3.-EFFECT OF TEMPERATURE DURING AIR TREATMENT IN A FLUID BED ON THE FSI, VOLATILE MATTER, AND OXYGEN CONTENT OF CHARS OF PITTSBURGH-SEAM COAL. RESIDENCE TIME IS ABOUT 40 MINUTES.

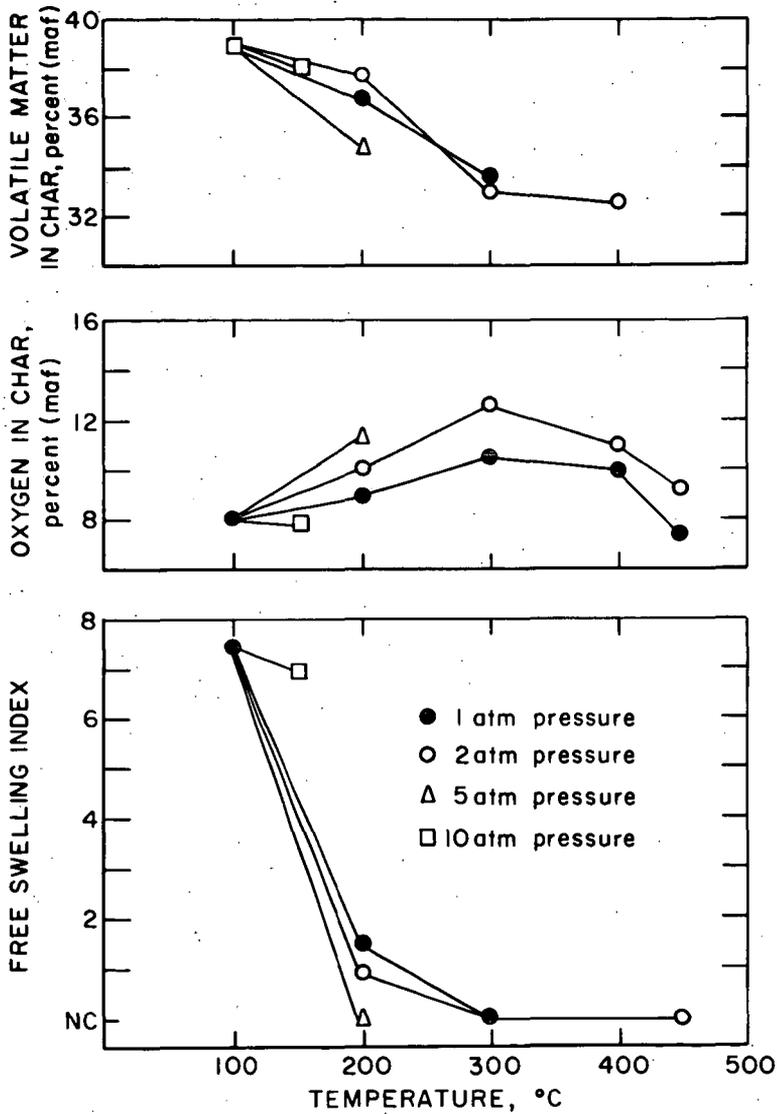


Fig. 4.-EFFECT OF PRESSURE DURING AIR OXIDATION IN A FLUID BED OF PITTSBURGH-SEAM COAL (150-200 MESH) ON FSI, VOLATILE MATTER, AND OXYGEN CONTENT OF CHAR. RESIDENCE TIME IS 40 MINUTES.

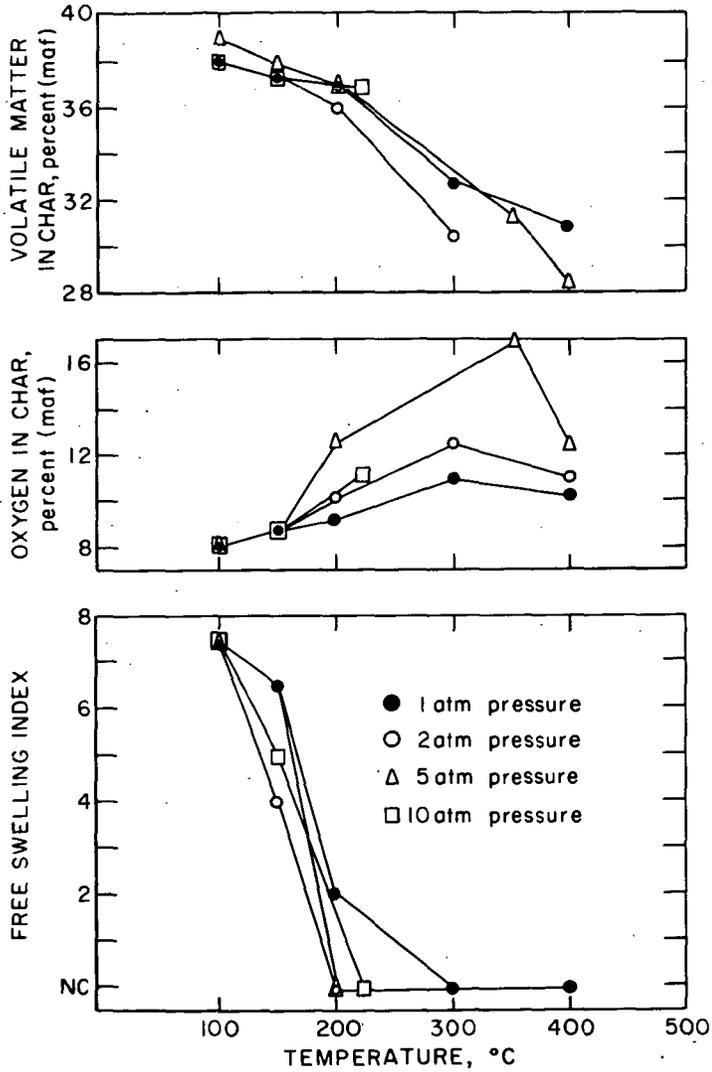


Fig. 5.-EFFECT OF PRESSURE DURING AIR OXIDATION IN A FLUID BED OF PITTSBURGH-SEAM COAL (150-200 MESH) ON FSI, VOLATILE MATTER, AND OXYGEN CONTENT OF CHAR. RESIDENCE TIME IS 20 MINUTES.

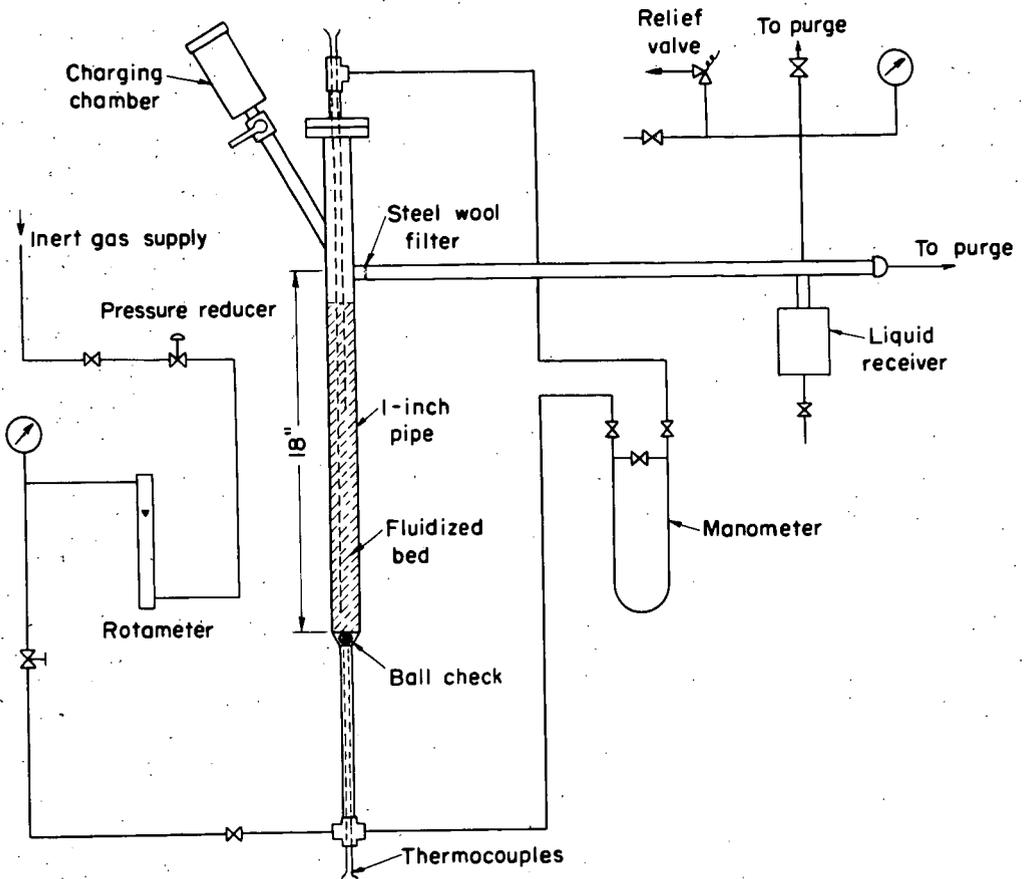


Fig. 6.-ONE-INCH REACTOR FOR CARBONIZATION TESTS

MOLTEN SALT CATALYSTS FOR HYDROCRACKING OF POLYNUCLEAR HYDROCARBONS

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INTRODUCTION

Intensive investigation has been underway for some time in the laboratories of Consolidation Coal Co. of various catalytic systems for the hydrocracking of coal "extract" to distillate oils. The extraction process and its integration with subsequent hydrocracking operations is described in several recent patents.⁽⁸⁾

Contact catalysts for hydrocracking of the extract have been extensively investigated in our laboratories both in batch and in small continuous hydrocracking units. The hydrocracking of coal extract using a contact catalyst in a three-phase fluidized system will be demonstrated on a 50 barrel/day pilot plant now being constructed at Cresap, W. Va.

Sulfur-resistant catalysts of the hydrofining type have given the most satisfactory results. These usually comprise a combination of the sulfides of Mo, Ni and Co on alumina gel support. Best results are obtained with large-pore alumina supports.

Rapid and efficient hydrogenolysis of the coal extract is effected at temperatures in the range of 800-825°F and at conversion levels up to about 60%.

The hydrogenated non-distillable residue from this operation, however, is much more refractory than the feed extract, and can be converted at practical rates only by raising the operating temperature. Although this is practical to do, the yield of the more valuable liquid products is lowered since the gas yield rises with increasing operating temperatures.

The limiting kinetic factor in the use of the "hydrofining" type catalyst is their very low cracking activity.

Dual function contact catalysts promoted by the use of acidic cracking agents were investigated to determine if they would be useful in conversion of the hydro residue. As the work to be reported below shows, this type of catalyst does not actually give improved performance since the acid sites are rapidly poisoned by the nitrogen content of the feed.

Attention was therefore turned to the development of a fused metal halide catalyst system.

The use of massive quantities of the catalyst was found to be desirable not only to develop the maximum hydrocracking activity but to "overwhelm" any nitrogen poisons in the feedstock. Fused salts were emphasized since the process under development visualizes continuous circulation of melt between hydrocracking and a regeneration operation where the nitrogen poisons would be removed.

The development of the massive fused salt catalyst system was initiated by a study of their activity in comparison with contact catalysts in the hydrocracking of hydro residue and a model polynuclear hydrocarbon: pyrene.

A voluminous literature exists on the use of metal halide catalysts in the hydrocracking of coal and coal tar. In many cases, the metal halide was not introduced directly as such but in all likelihood was generated in part in situ by reaction of a halogen promoter with the free metal or with a metal salt.

Excellent review articles^(17,18) and books^(8,11) are available summarizing this work so that there is no need to extensively discuss the original references.

In all of this work relatively small amounts of catalyst, i.e., less than 5 wt. % of the feed and generally of the order of 1 wt. % or less were employed. Under these conditions most investigators^(13,14,20) agree that halogen promoted tin catalysts are the most active of this class. The superiority of tin catalysts over zinc catalysts when used in small concentrations is further illustrated by the fact that there have been no commercial coal hydrogenation operations using zinc catalyst while there were commercial operations in both England^(4,7) and Germany⁽¹¹⁾ which used tin catalysts.

In addition, excellent results equal or superior to those with $ZnCl_2$ have been obtained with 1% nickelous chloride⁽¹⁹⁾ catalyst when proper methods of distribution of the catalyst on the substrate were used.

The above order of activity has no relationship to the cracking activity of these catalysts. Zinc chloride is well known as a Lewis acid type catalyst⁽³⁾ which has fairly good catalytic activity for most Friedel Crafts type reactions such as polymerization of olefins, alkylation of aromatic compounds with olefins, etc. It also is well known as a cracking catalyst and has been used, for example, for the catalytic cracking of shale oil.⁽⁶⁾

Stannous chloride, however, is not well known as an active Lewis acid although it does have electron accepting properties as evidenced by its formation of ammoniate complexes such as $SnCl_2 \cdot NH_3$. It is reported to have some catalytic activity of the Friedel Crafts type for reactions such as the polymerization of certain unsaturated compounds such as vinyl ethers,⁽¹²⁾ and the acetylation of olefins, i.e., reaction of acetic anhydride with 2,4,4-trimethyl pentene-1.⁽¹⁾ However, in general, it must be regarded as a very weak Friedel Crafts type catalyst with very little cracking activity as compared with $ZnCl_2$.

There is little or no evidence likewise that nickelous chloride has any substantial cracking or Friedel Crafts activity.

Weller⁽¹⁸⁾ has pointed out that there is sufficient sulfur in most of the feedstocks to decompose the metal halides, in the small quantities used, by the reaction



and therefore concludes that the halide is not the true catalyst. Rather he proposes that the catalyst is really a dual function one in that the HCl is a splitting or cracking catalyst while the tin acts as a hydrogenating component to stabilize the reactive fragments by reaction with hydrogen. In this respect, the point of view is quite similar to the commonly accepted mechanism of the action of dual function contact catalysts used for hydrocracking of petroleum feedstocks. In this latter case, the role of the hydrogenating metal is regarded⁽¹³⁾ as one of prevention of coke deposits by hydrogenation of highly unsaturated intermediates formed by catalytic cracking on the acid sites of the catalyst.

The above theory in the case of tin, however, is difficult to accept since there are no experimental facts with pure organic compounds which show that either tin metal or tin sulfide per se has any substantial hydrogenating activity.

It may be, as a matter of fact, that the unique position of tin chloride in the hydrogenolysis of coal is due to its known better thermodynamic stability towards decomposition by hydrogen sulfide as compared with zinc chloride, for example,

Equilibrium constants at 700°K for reaction (1) of SnCl₂ and ZnCl₂ with H₂S were calculated from available thermodynamic data with the results shown below:

$$K_M = \frac{P_{HCl}^2}{P_{H_2S}} \quad K_{Zn} = 400 \quad K_{Sn} = 1.5$$

It is thus clear that tin chloride is much more stable than zinc chloride and that under equivalent operating conditions with the same quantity of promoter, etc., that a much higher percentage of the tin will be present as tin chloride.

Thus, it appears possible that in contradistinction to the opinion expressed by Weller,⁽¹⁸⁾ the true catalyst is the small amount of undecomposed metal halide and that no dual function catalysis is involved.

Another object of the present investigation therefore was to obtain a better understanding of the catalytic activity of molten metal halides in hydrocracking processes. A pure compound, i.e., pyrene, was used to eliminate complications due to the interaction of the metal halide with hetero atom impurities and also to simplify analytical interpretation of the results. Massive quantities were used to insure the presence of a definite molten halide phase and because of the greater catalytic activity when massive quantities are used.

One of the points that was felt desirable to clarify was to what extent satisfactory operation and activation of hydrogen could be achieved with a molten halide catalyst without the addition of a separate hydrogenating component. The prior hydrocracking literature is not wholly clear on this point. There are, however, some references which showed that AlCl₃ and FeCl₃⁽¹⁰⁾ have definite catalytic activity for the hydrocracking of naphthalene. Only a small percent of catalyst was used such that no molten halide was likely present and rather severe conditions, i.e., 460°C for 3 hours were employed. Sixty percent conversion to single ring aromatic hydrocarbons was reported.

Similar results were obtained with anthracene although a lower yield of low boiling aromatics was obtained.

Winter and Free⁽²¹⁾ subsequently investigated the hydrocracking of naphthalene, anthracene and phenanthrene with FeCl₃ and AlCl₃ catalysts at hydrogen pressures of 190-250 atms. and temperatures in the range of 350-490°C. They observed the formation of significant quantities of pitchy condensation products as well as lower boiling aromatic liquids. Again, small quantities of catalyst were used.

Another pertinent reference is that of Schmerling and Ipatieff⁽¹⁶⁾ who showed that aqueous zinc chloride impregnated on alumina was an active catalyst for the hydrocracking of naphthalene.

Materials Used

Pyrene - Obtained from Gesellschaft Fur Teerverwertung MBH, m.p. = 149-151°C, b.p. = 393.5°C, purity = 98%. Typical analysis of the feedstock is shown in Table I.

Hydro Residue - The hydro residue used for runs in Table III was produced by hydrocracking a coal extract in a continuous fluidized bed unit using a nickel molybdate catalyst described below. The residue represents 29% of the extract fed and is free of material boiling below 400°C. The extract was obtained by extracting a high volatile bituminous coal from the Pittsburgh Seam, Ireland Mine, with tetralin, and amounted to 57% of the moisture- and ash-free coal. Some properties of the hydro residue are given in Table I.

Benzene - Fischer Scientific Co. Certified Reagent, Thiophene-free.

Catalysts

1. Nickel Molybdate on Alumina - A commercial hydrofining catalyst, containing 6.8% molybdenum, 3.8% nickel, and 0.1% cobalt supported on alumina gel. Unless otherwise noted, this catalyst was presulfided with 15% H₂S - 85% H₂ at 500°F. It has a surface area of 200 m²/g, a porosity of 77%, and an average pore diameter of 200 Å.
2. Fluorided Nickel Molybdate on Alumina - The above sulfided catalyst which was treated with 4 mole percent HF in nitrogen at 300°C until it consumed HF corresponding to 10% of its weight.
3. Nickel Molybdate on Silica-Alumina - Active metals corresponding to those in Catalyst No. 1 (6.8% Mo, 3.8% Ni, and 0.1% Co) were locally impregnated on Houdry S-90, a 12.5% alumina cracking catalyst with a surface area of 430 m²/g, a porosity of 65%, and an average pore diameter of 70 Å.
4. Zinc Chloride - Fisher Scientific Co. Certified Reagent, various lots 96.2 to 98.8% pure, dried before use by heating in a vacuum at 110°C. After this treatment, it contained 1 to 1.5% water and up to 1.8% ZnO.
5. Stannous Chloride - Fisher Scientific Co. Certified Reagent, SnCl₂·2 H₂O, heated before use at 150°C and 1 mm Hg pressure for 2 hours to remove water.
6. Aluminum Bromide - Fisher Scientific Co. Certified Reagent, Anhydrous, 99% pure.
7. Nickel Molybdate Catalyst Impregnated with Zinc Chloride - A solution of zinc chloride in methyl ethyl ketone was used to impregnate Catalyst No. 1, following the procedure used by Innes for determining catalyst porosity.⁽⁸⁾ The solvent was removed by heating at 60°C and atmospheric pressure overnight, followed by two hours at 200°C and 1 mm Hg pressure. The final catalyst contained 19% zinc chloride.
8. Zinc Chloride on Alumina - American Cyanamid gamma alumina stabilized with 2% silica was impregnated with 19% zinc chloride by the same procedure as for Catalyst No. 7. The alumina had a surface area of over 225 m²/g, and an average pore diameter of 80-100 Å.
9. Mixtures - Runs 2 and 3 were made with mixtures of Catalyst No. 1 and a salt catalyst. These were added separately to the autoclave.

Equipment

The basic unit for the hydrocracking tests was an American Instrument Co., Catalog No. 40-2150 rocking autoclave. The normal rocking motion of 36 cycles/sec. about the axis of the autoclave was found to give good catalyst mixing only if the catalyst was 35x65 mesh or finer. In order to test catalysts of 1/16-inch diameter such as were being used on continuous units, the autoclave and furnace were mounted on the end of a 12-inch arm, so that a shaking motion resulted rather than rocking. The autoclave was driven at 86 cycles/sec. through an angle of 30° at the end of the 12-inch lever arm as shown in Figure No. 1.

Other features of the test unit are evident from Figure No. 1. Hydrogen can be frequently added to the autoclave during the run to maintain pressure. Hydrogen consumption is measured directly by the change in pressure on the 300 ml accumulator. The accumulator is isolated from the compressor during a run and a precision Heise gauge indicates the pressure to ± 10 psi.

Procedure for Hydrocracking Tests

The 300 ml autoclave is weighed and 50 grams of feed plus the required weight of catalyst added. The autoclave is then closed, evacuated through valve V-2, and pressure tested with 1000-1500 psig of hydrogen from the accumulator. Heating is then commenced with V-3 closed.

When the temperature approaches the area where reaction will begin (ca. 300°C), V-3 is opened and the reactor pressure watched for evidence of hydrogen consumption. Hydrogen is thereafter supplied as needed in frequent increments from the accumulator until the full hydrogen pressure is reached when reaction temperature is reached. Thereafter, pressure is maintained, if necessary, by more hydrogen additions. The rate of temperature rise is controlled to average 10°C/min. to 375°C. From 375°C to the maximum temperature requires 5 to 15 minutes depending upon the temperature used and the extent of the exothermic reaction obtained. The temperature is then held at the desired level for a set time (usually one hour), and then lowered rapidly to 250°C via an air blast. After reaching 250°C, the motion is stopped, valve V-3 is closed, and the temperature maintained during depressuring of the lines. The line from the accumulator to the autoclave is disconnected at V-3 and replaced with the line (dashed) to the recovery train. The train is evacuated through V-4, and the contents bled off through a dry-ice-acetone cold trap, an Ascarite trap to remove acid gases, and into a gas holder.

Analysis of Hydrocracked Products from Runs Using Zinc Chloride

The gases passing through the cold trap from the 250°C bleed-off are metered and analyzed on a molecular sieve gas chromatograph column (Linde 5A, Medium Grade). The hydrogen gas remaining after the run is subtracted from that fed from the accumulator to give the overall hydrogen consumption for the run. The volatile materials in the cold trap are bled into an evacuated bottle by placing the cold trap in ice water until the sample bottle reaches 1 atm. The cold trap is then connected to an evacuated stainless steel bomb immersed in dry-ice-acetone and the original trap allowed to rise to room temperature. The volatile products collected in the glass sample bottle and the stainless bomb are subsequently analyzed for C₁ to C₇ hydrocarbons on a gas chromatograph (hexamethylphosphoramide supported on Chromosorb W). The light oil and water remaining in the original cold trap are separated and analyzed.

The product remaining in the autoclave at 250°C is removed after cooling to room temperature, using a mixture of organic solvent (carbon disulfide for pyrene runs, benzene for extract hydro residue runs) and water. The residue is repeatedly washed with water in a Waring Blender and filtered until free of chloride ion. The filtrates are separated into water and organic phases and each washed until water is free of organics and the organic phase free of chloride.

The filter cake from the final water wash is Soxhlet extracted with methyl ethyl ketone (MEK). The soluble fraction is combined with the organic filtrate phase and distilled.

The MEK-Insoluble material in the Soxhlet thimble includes zinc oxide and zinc sulfide as well as organic residue. The amounts of each are determined by analysis.

The procedures for tin chloride or combined catalyst runs followed the above format with very minor modifications. Where only a supported catalyst was involved, the procedure simplified to pressure filtration (20 psi), MEK extraction of the catalyst and sampling of the filtrates.

Product Boiling Range

Boiling ranges of the pyrene products were determined by gas chromatography using a silicone rubber column at 170°C with flame ionization detector. This permitted CS₂ to be used as a solvent for solid fractions without interference. A fairly simple pattern of about 20 peaks resulted.

Products from runs in which hydro residue was fed were vacuum distilled to give the distillate distribution because of the more complicated nature of the feed.

Hydrogen consumption is determined directly from hydrogen fed and recovered. Conversion is calculated by subtracting the recovered residue (+400°C) from the weight of feed and dividing the difference by the weight of feed.

A measure of the asphaltic nature of extracts and hydro residue (Table I) is given by solvent fractionation. "Benzene-Insolubles" is the fraction of extract insoluble in benzene at its atmospheric boiling point (Soxhlet apparatus). "Asphaltenes" is the benzene-soluble, cyclohexane-insoluble fraction, determined by mixing one part of benzene-soluble material with nine parts of benzene and 100 parts of cyclohexane, by weight, and filtering at room temperature. The fraction soluble in this mixture is termed "oil".

RESULTS AND DISCUSSION

Contact Catalysts with Cracking Promoters

The first approach used in attempting to enhance the cracking activity of the contact-type catalyst was to add cracking promoters. One method used was to incorporate the promoters in the contact-type catalysts either by impregnation with zinc chloride or by fluorination in the vapor phase with anhydrous hydrofluoric acid. Another method employed was to impregnate the hydrogenating metals on an active silica-alumina cracking catalyst base. Still another method was investigated in which the cracking catalyst, i.e., zinc chloride was not impregnated on the support but was simply added as a separate component to the autoclave. Finally, the use of a cracking catalyst by itself, i.e., zinc chloride impregnated on γ - Al_2O_3 was investigated without the addition of hydrogenating metals. The activity tests with pyrene feedstock are summarized in Table II. All runs were carried out at standardized conditions, i.e., a total hot pressure of 4200 psig and 1 hour residence time at the operating temperature of 427°C.

Runs 2 and 5 contained the same quantity of zinc chloride in each case, the only difference being that in the former case the zinc chloride was added as a separate component while in the latter case it was first impregnated on the nickel molybdate catalyst.

No detailed structural investigation was made of the products of the reaction. The boiling ranges of Table II, however, correspond roughly to the following classes of compounds as given below:

340 x 390°C	Partially Hydrogenated Pyrenes
280 x 340°C	Alkylated and Partially Hydrogenated Phenanthrenes
200 x 280°C	Alkylated and Partially Hydrogenated Naphthalenes
C_5 x 200°C	Alkyl Benzenes, Single Ring Naphthenes and Paraffins

In interpreting results, it should be noted that the hydrocracked product consists only of products boiling below 340°C. The pyrene is very readily hydrogenated such that in almost all cases very little remains completely unconverted.

In almost all cases an increase in hydrocracking activity was obtained by addition of the cracking promoter. This is evidenced by an increase in the yield of C_5 x 340°C distillate products as well as a substantial increase in the hydrogen consumption. A lone exception was stannous chloride. Here, the very low cracking activity of the metal halide was more than compensated for by a decreased activity of the contact catalyst. The latter may be due to coating of the contact catalyst with the molten salt. Zinc chloride, however, is such a strong cracking catalyst that it acts as a net promoter in spite of the fact that the same type of deactivation by coating of the

contact catalyst is possible here too. As a matter of fact, it appears to be slightly more active when added separately than when it is impregnated on the catalyst before use.

It is interesting to note that $ZnCl_2$ on Al_2O_3 , even without the hydrogenating metals, has hydrocracking activity although it is less than that of the nickel molybdate catalyst by itself. It also shows a relatively high coke yield which may possibly be attributed to the absence of hydrogenating metals. It is clear, however, as was shown by Schmerling and Ipatieff,⁽¹⁶⁾ that zinc chloride even in the absence of hydrogenating metals is capable of activating hydrogen for the hydrogenation and hydrocracking of polynuclear aromatic hydrocarbons.

The activities of the other two "dual function catalysts" investigated, i.e., fluorided nickel molybdate and Co-Mo-Ni on a cracking catalyst base (Houdry S-90) are also higher than that of the nickel molybdate catalyst and are even slightly more active than the zinc chloride promoted catalysts for total conversion. They produce, however, more middle range boiling distillates and less gasoline. The yield of $C_5 \times 200^\circ C$ distillate was 27.1% of the feed in the case of the zinc chloride catalyst and only 13.5% of the feed for the S-90 catalyst.

Ammonia Tolerance of Promoted Catalysts

The development of the dual function catalysts was aimed at their use, as mentioned above, in the hydrocracking of refractory residues from the hydrogenolysis of coal extract. These residues, as the data given in Table I show, contain substantial quantities of nitrogen of the order of 1 wt. % or more. Therefore, if these catalysts were to be of much use in such an operation, they must be relatively resistant to poisoning by NH_3 and other nitrogen bases released during the hydrocracking process.

The investigation was therefore directed towards determining the activity of these catalysts as a function of the partial pressure of NH_3 in the gas phase. In order to guide the experimental work, rough absorption isotherms for NH_3 were determined for two of the above catalysts, i.e., $ZnCl_2$ on nickel molybdate and Co-Mo-Ni on S-90. These are shown in Figure 2.

The results are at least roughly correct since the $350^\circ C$ isotherm for Catalyst No. 7 approaches the theoretical asymptotic value of 32 cc NH_3/gm . This value corresponds to the addition of 1 mole of NH_3 to 1 mole of $ZnCl_2$.

Experiments were now conducted in which controlled amounts of NH_3 were added such that the partial pressure of NH_3 could be estimated after correction for the amount absorbed on the catalyst.

The results for three types of catalysts are summarized in Figure 3 where yields of distillates are plotted as a function of NH_3 pressure. It is noted that even the nickel molybdate catalyst by itself suffers a loss of activity on addition of NH_3 . The S-90 catalyst appears to be able to tolerate somewhat larger quantities of NH_3 than the $ZnCl_2$ -impregnated catalyst probably because the acidic sites are weaker and are more readily dissociated. This fact is evident from the absorption isotherms given in Figure 2.

Thus, to obtain a substantial improvement in activity over the nickel molybdate catalyst, the NH_3 pressure must be maintained below about 5 psi for the $ZnCl_2$ promoted catalyst or slightly higher for the S-90 catalyst. To achieve such low partial pressures of NH_3 with high nitrogen feedstocks would require, in general, impractically high rates of hydrogen circulation. Consider a feedstock, for example, which releases 1 wt. % nitrogen as ammonia in a hydrocracking process wherein the hydrogen partial pressure is maintained at 200 atms. A hydrogen circulation rate of greater than 160 SCF/lb feed would be required in this case to maintain the partial pressure of NH_3 below 5 psia in the outlet gas.

Autoclave tests were run with the hydro residue itself wherein the S-90 catalyst was compared with the nickel molybdate catalyst. The results of these tests are shown in Table III. It is seen that the high nitrogen content of the feedstock as expected has poisoned the activity of the S-90 catalyst such that it is less active than the nickel molybdate.

The activity of fused zinc chloride catalyst itself with no support or other additive was tested in massive quantities on this same feedstock with the results shown in Table III. In spite of the fact that a lower temperature was used, the molten zinc chloride catalyst more than doubled the conversion and hydrogen consumption. The selectivity of the process as measured by the quantity $(C_1-C_3) \times 100/\text{conversion}$ is also improved with the molten zinc chloride catalyst. C_1-C_3 here refers to the weight percent yield of methane, ethane plus propane.

Very noteworthy, likewise, is the high selectivity of the process for production of gasoline. Ninety-one percent of the distillate oils (b.p. below 400°C) boil in the gasoline range in the case of the $ZnCl_2$ catalyst, and only 52 percent in the case of the nickel molybdate catalyst.

Another distinctive feature of catalysis with massive quantities of zinc chloride is the high ratio of iso paraffins to n-paraffins produced as evidenced by the ratio of isobutane to n-butane of over 6/1. This phenomenon is observed with conventional "dual function" hydrocracking catalysts when the feedstock is free of nitrogen poisons. In this case the same phenomenon is observed by "over whelming" the nitrogen poisons with an excess of catalyst.

In contradistinction runs 8 and 9 using contact catalysts show a low ratio of iso to n-butane indicating that the acid cracking sites have been poisoned by the nitrogen bases in the feedstock.

These results point to the clear superiority of massive zinc chloride melts as a hydrocracking catalyst. The development is proceeding with the central concept of continuously circulating the molten halide catalyst to a regeneration step where the nitrogen poisons would be removed. Data on the effect of basic nitrogen on catalyst activity will be given in a subsequent paper.

Activity Tests of Molten Halide Catalysts with Pyrene Feedstock

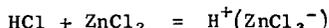
A series of further tests were made with pyrene feedstock to provide more background information for development of the molten halide catalyst system. Experiments were conducted to further clarify the effect of the quantity of catalyst used, the effect of the addition of cracking and hydrogenation promoters as well as a comparison of the activity of fused zinc chloride with other molten halide salts. The experimental results are summarized in Table IV.

It is noted that when the zinc chloride catalyst is used in relatively small amounts (in 7 percent by weight of the pyrene feed, Run 11), that the activity is quite low. The main reaction appears to be hydrogenation of pyrene to partially hydrogenated pyrenes with some hydrocracking to light distillates. The extent of hydrocracking is also much less than when the same amount of zinc chloride is used dispersed on an alumina support (cf. Run 7, Table II). However, when massive quantities of zinc chloride melt are used, i.e., Run 12, the hydrocracking of pyrene proceeds very vigorously. A much greater degree of hydrocracking is obtained than with any of the promoted contact catalysts discussed above. The result is also quite similar to that observed when massive quantities of zinc chloride melt were used for hydrocracking of extract residue (cf. Run 10, Table III). The characteristic high ratio of iso to n-butane (5.6/1) and high proportion of gasoline boiling range liquid, i.e., 91%, in the total $C_5 \times 340^\circ C$ distillate is again observed.

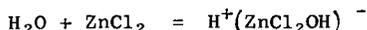
The coke plus tar yield was rather high in Run 12, i.e., 7.5% of the feed in spite of the relatively high pressure employed. Runs 13 and 14 were conducted to determine

if the addition of hydrogenating components to the melt, i.e., SnCl_2 and MoO_3 would reduce the coke plus tar yield. Stannous chloride in the small amounts used was completely inert, i.e., no difference in results is apparent between Runs 12 and 13. Molybdc oxide (Run 14) did increase the hydrogen consumption and decrease the gas yield slightly, but actually caused an increase rather than a decrease in tar plus coke yield.

Runs 15 and 16 were conducted to determine what the effect of the addition of cracking promoters to the melt would be. HCl potentially can form the unstable Friedel Crafts acid by the reaction,



while water can undergo a similar reaction,



The original melt was not completely anhydrous and usually contained about 1 wt. % H_2O . Thus, the addition of further quantities of water can increase the amount of acidic cracking catalyst by the above reaction.

It is seen that the addition of HCl is unfavorable in that it causes a large increase in the amount of coke. Water addition on the other hand increased the overall hydrogen consumption with only a slight increase in the amount of tar plus coke.

Run 17 was conducted to determine whether massive quantities of stannous chloride melt would behave similarly to zinc chloride. It is seen that it is a very weak catalyst and that practically no hydrocracking takes place. The only process observed is hydrogenation to partially hydrogenated pyrenes. It would appear that the relatively good activity of tin catalysts for hydrogenolysis of coal and coal extract must in some way be related to their activity with respect to scission of specific weak bonds that are not present in pyrene or its partially hydrogenated homologues.

Finally, one experiment (Run 18) was conducted using massive quantities of an AlBr_3 melt. Due to the very high activity of this catalyst, it was not possible to run at comparable conditions used for the ZnCl_2 catalyst. The experiment was run at a much lower temperature, i.e., 300°C ; and a lower pressure, i.e., 3000 psig. As a matter of fact the absorption of hydrogen was initially so rapid that the pressure fell considerably below 3000 psig at first. This may be the reason for the fairly high yield of tar obtained.

It is obvious, however, that AlBr_3 is a much more active catalyst than zinc chloride. The conditions chosen were too severe in that, outside of the tar produced, the feed pyrene was almost completely degraded to low molecular weight paraffins in the range of C_1 to C_6 . The $\text{C}_5 \times 150^\circ\text{C}$ distillate, as determined by gas chromatography, showed the composition given below:

	Wt. % of Cut
Isopentane	48.2
n-Pentane	18.2
2,2-Dimethyl Butane	1.8
2,3-Dimethyl Butane)	
2-Methyl Pentane)	8.2
3-Methyl Pentane	3.7
n-Hexane	2.5
Methyl Cyclopentane	0.4
$\text{C}_7 +$	18.0
Total	100.0

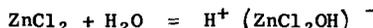
The zinc chloride catalyst is almost completely inactive for hydrocracking of single-ring aromatic hydrocarbons as the data of Table V show where benzene is used as a model compound. This is one reason that high yields of gasoline boiling range hydrocarbons are obtained with zinc chloride melt catalyst. In other words, the hydrocracking process is suspended after aromatic hydrocarbons boiling in gasoline range are produced. Other experiments showed that the whole gasoline fraction including aromatics, naphthenes and paraffins are resistant to further hydrocracking by zinc chloride catalyst.

This is not true of aluminum halide catalysts since it is clear that continued hydrocracking to produce predominantly propane and butanes occurred under the conditions used. The effect of using milder operating conditions with aluminum halide catalysts is now being investigated.

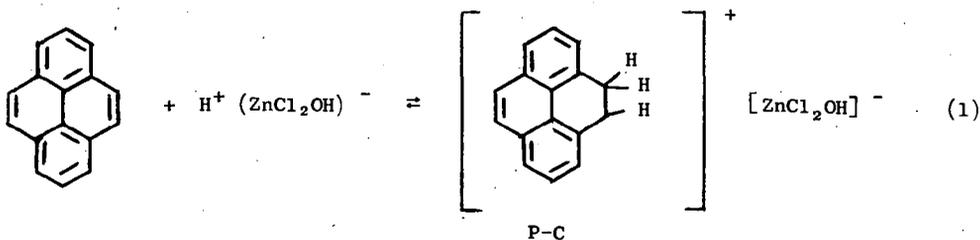
Mechanism of Hydrocracking with Molten Halide Catalysts

The investigation was not aimed at specifically unravelling the mechanism of the hydrocracking process so that one can only speculate on this question.

The nature of the active catalyst is not clear but is likely a Friedel Crafts acid. As stated above, no precautions were used to completely dehydrate the zinc chloride melts used and they usually contained about 1 wt. % of water. Thus, the active catalyst may be the acid produced by interaction of zinc chloride with water

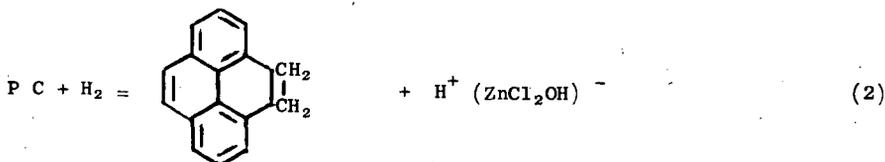


The first step in hydrocracking is likely the addition of the Friedel Crafts acid to the labile unsaturated bond between the 9 and 10 carbon atoms of the pyrene ring.



This is similar to the first step in the mechanism proposed by Schmerling⁽¹⁵⁾ and others for alkylation of isoparaffins with olefins using Friedel Crafts catalysts.

The aromatic-catalyst complex, written as P C, can then react with hydrogen to regenerate the catalyst and produce 9,10-dehydropyrene as follows:



This basic mechanism for hydrogenation can continue for further absorption of hydrogen, scission reactions leading to ring opening and dihydroalkylation, etc.

Experiments were carried out to determine the miscibility of $ZnCl_2$ and pyrene in one another. After mixing an equal weight of the two components at $350^\circ C$, no appreciable separation of phases could be detected on standing for one hour. Whether one is dealing with a true solution or relatively stable emulsions is not certain at this time.

The high dependence of reaction rate on catalyst concentration would not be surprising if one is dealing with a homogenous solution of catalyst and hydrocarbon reactant.

It is not clear at present whether the results reported here are unique to molten halide Friedel-Crafts catalysts. It is possible that similar results can be obtained with some liquid protonic acids such as phosphoric acid, hydrofluoric acid, hydroxy fluoboric acid, etc., once proper conditions are selected. Experiments are now in progress to check these possibilities. Preliminary results indicate that phosphoric acid is inactive for hydrocracking of pyrene at $300^\circ C$ and 3000 psig hot pressure.

ACKNOWLEDGMENT

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TABLE I

Analysis of Feedstocks

<u>Feed</u>	<u>Pyrene</u>	<u>29% Residue (+400°C) from Extract Hydrogenation</u>
H	4.94	6.82
C	94.87	90.79
N	0.02	1.17
O	0.06	1.07
S	0.11	0.15
Benzene-Insolubles	--	3
Asphaltenes	--	30
Oil	--	67

TABLE II

Comparison of Activity of Various Contact Catalysts
Effect of Promotion with Acid Cracking Catalysts

Hydrocracking of Pyrene at 427°C and 4200 psig Hot Pressure
Residence Time at Temperature = 60 min.

Run No.	1	2	3	4	5	6	7
Contact Catalyst	Sulfided Nickel Molybdate	ZnCl ₂	SnCl ₂	Fluorided Nickel Molybdate	ZnCl ₂ on Nickel Molybdate	Co-Mo-Ni on S-90	ZnCl ₂ -Al ₂ O ₃
Other Catalyst	None	ZnCl ₂	SnCl ₂	None	--	--	--
Contact Catalyst (Wt. Ratio) Pyrene	0.30	0.30	0.30	0.30	0.37	0.30	0.37
Other Catalyst (Wt. Ratio) Pyrene	0	0.07	0.07	0	--	--	--
Yields, Wt. % of Pyrene Feed							
CH ₄	0.0	0.4	0.2	0.0	0.4	0.2	0.5
C ₂ H ₆	0.3	1.3	0.8	0.2	1.2	0.6	1.4
C ₃ H ₈	0.7	1.7	1.4	0.5	1.3	1.1	1.6
C ₄ H ₁₀	0.0	0.6	0.1	0.2	0.3	0.5	0.5
C ₅ x 150°C Dist.	2.7	15.8	2.9	5.8	22.1	6.4	4.1
150 x 200°C Dist.	0.0	8.4	1.3	0.2	5.0	7.1	2.2
200 x 280°C Dist.	27.1	17.5	11.1	9.3	11.4	15.4	8.5
280 x 340°C Dist.	18.7	20.5	15.8	68.5	16.3	45.9	16.8
340 x 390°C Dist.	52.6	35.6	59.9	21.4	42.7	26.8	47.4
Pyrene	2.6	1.9	9.0	0.0	3.2	0.6	13.6
Coke on Catalyst	0.6	2.8	1.6	0.9	2.1	1.9	7.0
Total Including H Consumed	105.3	106.5	104.1	107.0	106.0	106.6	103.6
H Consumed, Wt. %	5.33	6.56	4.12	6.98	5.98	6.62	3.56

TABLE III

Comparison of Contact Catalysts with ZnCl₂ Melt for Hydrocracking of Extract Hydro Residue

Total Pressure = 4200 psig - Residence Time at Temperature = 60 min.

Run No.	8	9	10
Catalyst	Co-Mo-Ni on S-90	Sulfided Nickel Molybdate	ZnCl ₂ Melt
Temperature, °C	441	441	427
Catalyst/Feed, Wt. Ratio	0.3	0.3	1.00
<u>Yields, Wt. % MAF Feed</u>			
CH ₄	1.1	1.1	1.2
C ₂ H ₆	1.2	1.2	1.5
C ₃ H ₈	1.6	1.6	4.6
iC ₄ H ₁₀	0.2	0.1	5.0
nC ₄ H ₁₀	1.0	1.2	0.8
C ₅ x 150°C Dist.	7.0	9.1	52.5
150 x 200°C Dist.	1.7	8.4	10.4
200 x 400°C Dist.	16.9	16.1	6.3
MEK-Sol. + 400°C Residue	67.5	60.2	19.0
MEK-Insol. + 400°C Residue	2.9	2.4	3.4
Conversion, Wt. % Feed	29.6	37.4	77.6
H ₂ Consumed, Wt. % Feed	2.64	3.14	6.85
(C ₁ -C ₃) x 100/Conversion	13.4	10.5	9.5

TABLE V

Hydrocracking of Benzene with Zinc Chloride Catalyst

Temperature = 427°C - Residence Time at Temperature = 60 min.

Total Hot Pressure = 4200 psig

Yields, Wt. % of Benzene Feed

CH ₄	-	.04
C ₂ H ₆	-	.09
C ₃ H ₈	-	.92
iC ₄ H ₁₀	-	.43
nC ₄ H ₁₀	-	.14
C ₅ H ₁₂	-	.24
Other C ₆ 's	-	.42
Benzene	-	<u>99.00</u>
Total		101.28

H₂ Consumed = 0.94 wt. %

TABLE IV

Comparison of Molten Salt Catalysts for Pyrene Hydrocracking

All Runs - 60 min. Residence Time at Temperature

Run No.	11	12	13	14	15	16	17	18	
Temperature, °C	427	↔							300
Total Hot Pressure, psig	4200	↔							3000
Catalyst	ZnCl ₂	↔							SnCl ₂ AIBr ₃
Catalyst/Pyrene, Wt. Ratio	0.07	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
Catalyst Additive	None	None	SnCl ₂	MoO ₃	HCl	H ₂ O	None	None	
Additive/Pyrene, Wt. Ratio	--	--	.02	.05	.021	0.08	--	--	
Yields, Wt. % Pyrene									
CH ₄	0.0	0.8	0.8	1.0	2.3	1.0	0.0	1.8	
C ₂ H ₆	0.1	1.4	1.6	2.3	4.3	2.3	0.2	1.8	
C ₃ H ₈	0.5	11.2	11.4	9.7	11.1	10.6	0.2	25.2	
iC ₄ H ₁₀	0.6	9.6	9.8	8.1	8.5	8.2	0.0	24.1	
nC ₄ H ₁₀	0.1	1.7	1.6	1.2	1.8	1.1	0.0	19.1	
C ₅ x 150°C Dist.	6.3	52.7	52.4	53.2	45.3	{ 0.0		24.5	
150 x 200°C Dist.	0.3	1.7	1.8	2.1	1.3	{ 66.8		--	
200 x 280°C Dist.	2.0	1.9	2.7	6.2	1.6	{ 0.9		--	
280 x 340°C Dist.	1.0	3.3	3.3	4.7	0.9	{ 3.0		--	
340 x 390°C Dist.	36.8	11.5	12.2	7.2	0.6	{ 11.8		--	
Pyrene	53.1	6.5	4.8	2.4	0.4	{ 49.9		--	
+Pyrene	--	2.5	2.7	3.1	9.1	{ 3.6		0.0	
Coke	--	5.0	4.2	8.6	21.5	{ 4.8		0.0	
Total	101.2	109.2	109.3	109.8	108.7	110.2	101.8	112.4	
H ₂ Consumed, Wt. % Pyrene	1.23	9.21	9.31	9.85	8.68	10.23	1.8	12.4	

Figure 1
FLOW DIAGRAM
FOR AUTOCLAVE UNIT

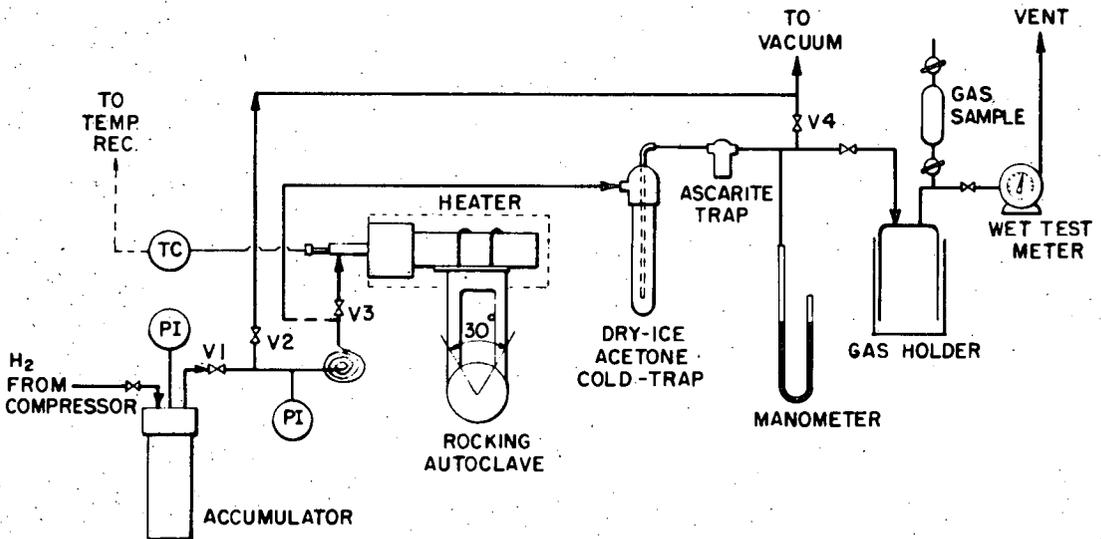


FIGURE NO. 2

Ammonia Adsorption Isotherms

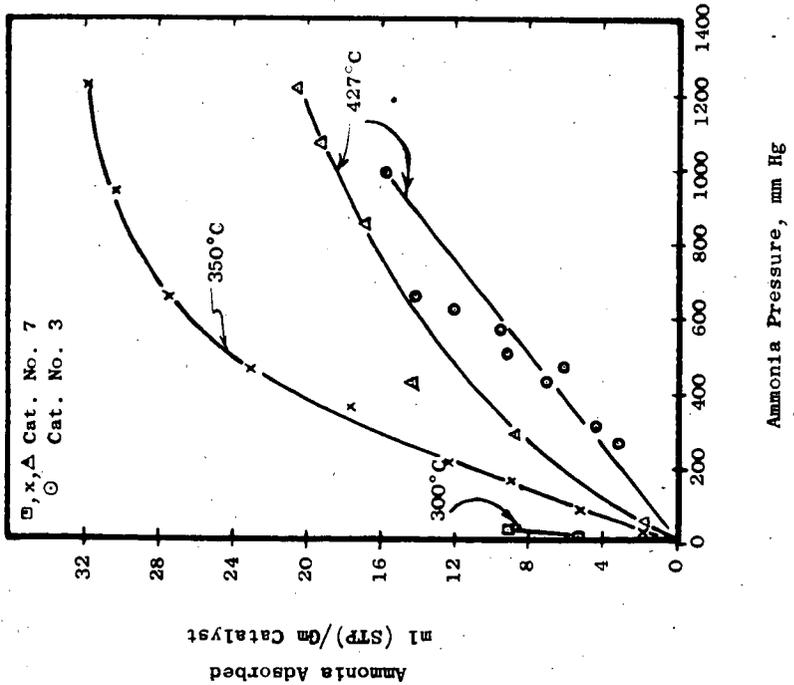
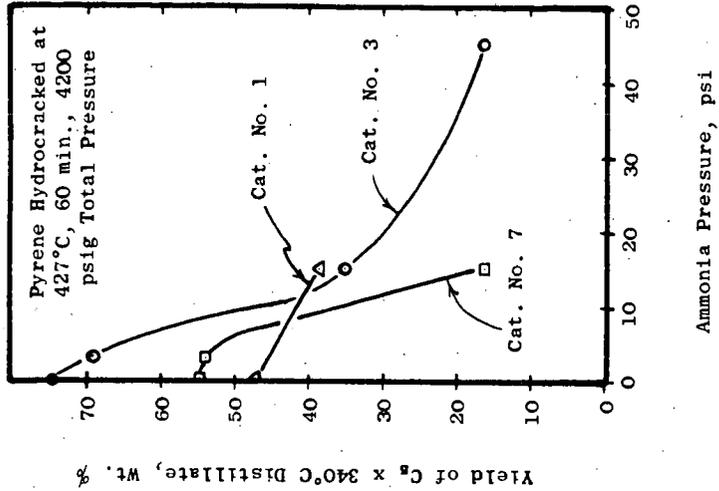


FIGURE NO. 3

The Effect of Ammonia
Partial Pressure on
Distillate Yields



MOLTEN ZINC HALIDE CATALYSTS FOR THE HYDROCRACKING OF COAL EXTRACT AND COAL

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INTRODUCTION

The background information leading to the development of fused metal halide catalysts for the hydrocracking of coal extract was discussed in a previous paper.⁽¹⁰⁾ It was shown, therein, that metal halides which are strong Lewis acids are active catalysts for the hydrocracking of polynuclear hydrocarbons and residues from the hydrocracking of coal extract with contact catalysts.

The present paper describes the initial steps in the development of molten zinc chloride catalysts for the hydrocracking of coal extract and even coal itself. An extensive survey of the variables in the hydrocracking of coal extract with massive quantities of zinc chloride melt is presented. Comparative data are also presented with other catalyst systems. All data given here were obtained in batch autoclave experiments.

In addition to the zinc halides, several possible Lewis acid catalysts were considered such as AlCl_3 , AlBr_3 , BF_3 , etc. These were rejected primarily because they would be completely destroyed by the steam released during the hydrogenation of coal extract. Also, as a consequence of the halogen acids released during hydrolysis of the catalyst, these materials would be much too corrosive to be useful in potential commercial systems.

Zinc bromide was found to be equivalent in activity to zinc chloride. It was rejected from further consideration because of cost.

Zinc chloride has been widely used as a catalyst in experimental work in coal hydrogenation although it has never been employed in commercial plants. No literature data are available on its activity for the hydrocracking of coal extract.

Small amounts of catalyst⁽⁹⁾ of the order of 3 wt. % or less of the coal were used and frequently the catalyst was impregnated on the coal before use. There appears to be no record of the use of massive quantities of molten zinc chloride catalyst in the coal hydrogenation literature.

ZnCl_2 almost universally has been regarded as being inferior in activity to SnCl_2 or halogen-promoted tin compounds^(2,5,7,8,9) as a catalyst for coal hydrogenation. One exception to this is found in some Japanese work,⁽⁶⁾ on hydrogenating coal to heavy oil at the relatively mild operating conditions of 410°C and 200 atm.

The work was carried out on a fairly large pilot plant scale using 1% of zinc chloride and other catalysts. Zinc chloride was found to be the best catalyst of these tested including tin.

EXPERIMENTAL

The basic unit used in this work was a 300 ml shaking autoclave. This unit and the procedures involved have been described previously.⁽¹⁰⁾ One added feature used in two series of runs at constant hydrogen pressure was the use of a palladium probe. A palladium tube, 1/8-inch I.D., .010" wall and 7 inches long from J. Bishop and Co., was inserted into the autoclave and suitably connected to a gauge to read hydrogen pressure. The ends were silver soldered and the interior of the tube nearly filled with a stainless steel wire for support. At temperatures of 750°F and above, diffusion of hydrogen through the tube was rapid enough to give adequate response to changing pressure. A new tube was used each time to ensure freedom from sulfur poisoning, although burning off between runs was also found to restore activity. The probe was protected from splashing autoclave contents by baffles.

The feedstock for most of this work was "standard" extract prepared by continuous extraction of Pittsburgh Seam coal, Ireland Mine. Tetralin solvent was used with a residence time of 46 minutes at 380°C. Unextracted coal and ash were removed by filtration of the extractor effluent in a pressure filter at 200°C. The final extract represents 53% of the MAF coal. Properties are given in Table I.

The zinc chloride used was Fisher Scientific Co. Certified Reagent, 96-98% pure, dried before use by heating in a vacuum at 110°C. After this treatment, it contained 1-1.5 wt. % water and up to 1.8 wt. % zinc oxide.

The nickel molybdate catalyst is a commercial hydrofining catalyst containing 6.8% molybdenum, 3.8% nickel, and 0.1% cobalt supported on alumina gel. It has a surface area of 200 m²/g, a porosity of 77%, and an average pore diameter of 200 Å. It was used as 1/16-inch diameter beads, presulfided with 15% H₂S-85% H₂ at 500°F.

The extent of reaction of zinc chloride with nitrogen and sulfur was determined by elementary analyses. The work-up procedure for product analysis was as described previously.⁽¹⁰⁾ All the inorganic nitrogen was found in the water washings and was analyzed as NH₃ by distillation after adding caustic. The NH₃ is assumed to be present as ZnCl₂·xNH₃ or ZnCl₂·yNH₄Cl. The chlorine present in excess of that required for ZnCl₂ is assumed to be in the form of the double salt; ZnCl₂·yNH₄Cl. All of the sulfur in the MEK-insoluble fraction is assumed to be ZnS.

The analysis of the gasoline for individual saturated components was carried out by gas chromatography after suitable calibration with pure hydrocarbons. A temperature programmed stainless steel capillary column 0.02" dia. by 300' long coated with squalene was used in conjunction with a hydrogen flame ionization detector.

The analysis for individual aromatic hydrocarbons was carried by first isolating the aromatic fraction of the gasoline by liquid displacement chromatograph using silica gel as the absorbent. The aromatic fraction was then analyzed by gas chromatography in the same capillary column coated with 2,5-xyleneol phosphate.

RESULTS AND DISCUSSION

Comparison with Other Catalysts and Effect of Catalyst/Extract Ratio

Table II gives a comparison of three types of catalysts at low catalyst concentrations between 1 and 2.5 percent of the extract fed. The literature on coal hydrogenation which states that tin chloride in small concentrations is a superior catalyst is confirmed. In spite of the lower concentration of catalyst used and lower pressure, the tin catalyst gave the highest conversion and highest selectivity for production of liquid products. However, in view of the high cost of tin and its low activity for pyrene hydrocracking when used in massive quantities,⁽¹⁰⁾ no further test work was done with massive quantities of SnCl₂ in extract hydrocracking.

The activity of the nickel molybdate hydrofining catalyst increases markedly with increasing catalyst concentrations. Extra conversion tends to level off, however, as the catalyst extract ratio is increased beyond 0.3. These data are illustrated in Figure 1.

Two important features are evident from Figure 1. One is that conversion with the molten zinc chloride catalyst at a comparable catalyst extract ratio is always higher than with the contact catalyst type system and that the conversion reached at high catalyst extract ratios is much greater with the molten zinc chloride catalyst system. Another important feature illustrated in Figure 1 is the high conversion to gasoline boiling distillates obtained with the zinc chloride catalyst system. This especially becomes apparent at high catalyst to extract ratios, i.e., above about 0.3. This again is in distinction to the results obtained with the contact catalyst system where the gasoline range boiling distillates always comprised only a minor fraction of the total distillate oils produced. Thus, an important potential advantage of the molten zinc chloride catalyst system is the possibility of obtaining single-stage direct conversion of coal extract to high octane gasoline.

Figure 2 gives another comparison of results obtained under comparable conditions between the two catalyst systems. Especially interesting here is the rapid increase in the isobutane-to-normal butane ratio with increasing $ZnCl_2$ -to-extract ratio. At high catalyst/extract ratios gasoline is produced which contains a very high proportion of isoparaffins quite comparable to what is normally produced by hydrocracking of hydrofined petroleum feedstock with dual function contact catalysts. The isobutane-to-normal butane ratio is always higher than with the hydrofining catalyst system as illustrated at the bottom of the figure. This shows that no acid cracking function exists in the case of the hydrofining catalyst system. The sharp inflection point on the isobutane-to-normal butane ratio occurs at a catalyst ratio of about 0.3.

The data shown in Figure 2 illustrate that a high selectivity in conversion of extract to gasoline is possible with massive quantities of zinc chloride. The selectivity here is measured by the percent by weight of the extract that is converted to C_1 through C_3 hydrocarbon gases. At very high catalyst:extract ratios the gas yield becomes fairly large, but this would be reduced in an actual continuous system by continuous removal of the products to prevent further cracking of the gasoline components. It is also noted that, at catalyst extract ratios up to about .4, the selectivity is better than obtained with the hydrofining catalyst system. The experiments with the hydrofining catalysts were with fresh catalyst not contaminated with ash and carbon such that the activity is substantially greater than one would have in an actual practical system.

Effect of Residence Time, Temperature and Pressure

The influence of these variables with a constant zinc chloride/extract ratio is illustrated in Figures 3, 4, and 5, respectively.

Figure 3 again illustrates the higher conversion rates that can be obtained with molten zinc chloride catalysts as compared with the hydrofining catalyst system. Three hours are required to reach a conversion of 75% with the hydrofining catalyst system, as compared with less than 5 minutes residence time required to reach the same conversion level with the molten zinc chloride catalyst.

Figure 4 gives a very rapid survey of the effects of temperature and pressure on extract conversion with zinc chloride catalyst. It is seen that substantial conversions can be achieved even at low pressures (of the order of 2000 pounds) at quite low temperatures. It also appears that at low temperatures the conversion achieved may not be too sensitive to the actual pressure. Thus, by operating at

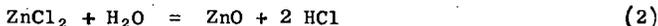
very low temperatures of the order of 650°F, substantial conversions can be achieved even at very low pressures perhaps as low as 1500 pounds. This remains to be confirmed by future work.

Figure 5 shows the effect of operating temperature at constant time and pressure on the single stage gasoline yields, i.e., the fraction of the total liquid product which boils within the gasoline range. It also shows the effect of operating temperature on selectivity of the process. It is seen that the gasoline yield increases with operating temperature, but even at temperatures as low as 625°F more than half of the liquid product boils within gasoline range. Thus, in any case, it would appear to be possible to recycle the heavier liquid to obtain ultimate conversion of all distillate products to gasoline. It is seen also that the selectivity of the process becomes better as temperature of operation is reduced, and that accordingly the ultimate gasoline yields, upon recycling of higher boiling liquids to extinction, would be very high at temperatures below about 760°F.

Reactions of Catalyst With Hydrocracked Products

The coal extract is rich in hetero atoms, i.e., N, O, and S, as the analyses of Table I shows. These are released during hydrocracking in the form of NH₃, H₂O and H₂S, respectively.

The following reactions with the catalyst are then possible:



The equilibrium constant for reaction (1) has been determined experimentally by Kapustinsky,⁽¹⁾ and that for (2) may be calculated from available thermodynamic data on zinc compounds⁽³⁾ with results given below:

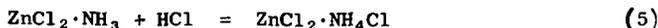
$$\log K_2 = \log \frac{P_{\text{HCl}}^2}{P_{\text{H}_2\text{O}}} = \frac{-6930}{T} + 8.03 \quad (4)$$

The dissociation pressure of NH₃ over zinc chloride melts has been measured by Krasnov.⁽⁴⁾

The equilibrium data of Kapustinsky⁽¹⁾ for reaction (1) indicates that nearly quantitative absorption of H₂S to produce ZnS should take place. This was confirmed experimentally, in that no H₂S could be detected in the product gas, and all of the sulfur released was absorbed by the melt.

The data for reaction (2) indicates that zinc chloride should be quite resistant to hydrolysis but that a small amount of HCl should be present in the gas. Experimentally nothing more than trace quantities of HCl could ever be found. The discrepancy may be due to a high degree of absorption of water by the melt which reduces the partial pressure of steam to a low value.

Krasnov's data⁽⁴⁾ indicate that the NH₃ pressure over melts containing less than 25 mole percent of ammonia would be quite small at temperatures in the normal range used for hydrocracking. Quantitative absorption of ammonia by the melts is thus to be expected, which was, in fact, confirmed experimentally. It is usual in the hydrocracking of standard extract to produce at least one mole of NH₃ for each mole of hydrogen chloride formed by reaction (1). The hydrogen chloride so produced is absorbed by the melt by the following reaction:



Equilibrium data for reaction (5) will be presented in a subsequent paper.

The melt fed to the autoclave experiments usually contained 2.5 to 3.0 mole percent of ZnO as determined by the ability of the anhydrous melt to chemically react with hydrogen chloride to produce water. The ZnO, of course, reacts with hydrogen chloride released by reaction (1) during hydrocracking by reversal of reaction (2). It is possible to add sufficient ZnO to neutralize all of the HCl produced. In this case no NH_4Cl would be formed in the melt. The ZnO acceptor for HCl can be produced during regeneration of the melt, for example, by oxidation of the ZnS formed by reaction (1).

Effect of NH_3 and NH_4Cl on Melt Activity

It is, therefore, clear that depending upon operating conditions used and whether or not zinc oxide acceptor is employed, both ammonia and ammonium chloride in widely ranged proportions can be present in the melt during hydrogenation. It is therefore of interest to see what effect these materials have on the hydrocracking activity of zinc chloride melt toward extract. The data in Figure 6 illustrate this point.

In these runs, the temperature and pressure were held constant at 750°F and 3000 pounds, respectively, and the amount of ammonia or ammonium chloride added was varied. It is seen that with both ammonia and ammonium chloride there was a decrease in extract conversion, but that the decrease is much more rapid in the case of ammonia than in the case of ammonium chloride.

Another interesting item illustrated in Figure 7 is the effect of ammonia and ammonium chloride addition on selectivity. It is seen that both additives have a favorable effect on this count in that they caused a very dramatic decrease in the gas yield. The effect of other additives was also studied, in particular the effect of the addition of zinc oxide. Zinc oxide prevents the formation of ammonium chloride by absorbing the HCl produced. Zinc oxide was found to have marked inhibiting effect when used in large quantities. The inhibiting effect is quite moderate when only small quantities are used.

The data of Figure 6 were obtained with a zinc chloride/extract weight ratio of 2. Similar data were obtained at other feed ratios of 1 and 3, respectively. Conversions were slightly lower when the feed ratio was lowered, particularly when the amount of NH_3 added was small. The major effect of the zinc chloride/extract ratio at low NH_3 concentrations was that the gas yield decreased rapidly as the feed ratio decreased.

When higher concentrations of NH_3 were used, there was no perceptible effect of feed ratio in the range of 1 to 3.

It is therefore concluded that one controlling factor in determining the amount of melt circulation required in an extract hydrocracking process is the accumulation of nitrogen poisons. It would appear from the prior experience with pyrene,⁽¹⁰⁾ however, that even with a feed low in nitrogen poisons that there is a kinetic advantage in the use of massive quantities of catalyst. The present data indicate, however, that no further advantage is gained by increasing the weight ratio of catalyst to feed beyond 1.

It is abundantly clear, therefore, that a commercial process for hydrocracking with zinc chloride melts would require continuous regeneration to remove the nitrogen poisons. Methods of regeneration will be discussed in a subsequent paper.

Some data on the effect of NH_3 at higher temperatures, i.e., at 800°F were also obtained. They are summarized in Table III. Under these conditions a small amount

of NH_3 , i.e., 0.09 mole percent has a favorable effect, in that the conversion is increased, the selectivity is greatly increased because of the lower gas yield and the yield of MEK-Insolubles is decreased. As a matter of fact, the increase in conversion due to NH_3 addition can be ascribed entirely to the decrease in the MEK-Insoluble yield. It appears likely that the favorable effect of small amounts of NH_3 is due to moderation of the cracking activity of the melt which is too high for best results at the conditions used. Even larger quantities of ammonia possibly could be tolerated with favorable results at temperatures above 800°F .

It is noted that at a 1/1 mole ratio of $\text{NH}_3/\text{ZnCl}_2$ the hydrocracking activity is reduced to about the equivalent to that obtained when only 2 percent of ZnCl_2 (with no NH_3 added) is used (cf. Table II).

Further addition of NH_3 decreases the catalytic activity of the melt even further. The data for the melt containing 2 moles $\text{NH}_3/\text{mole ZnCl}_2$ indicates that at this level the catalytic activity is almost completely poisoned.

The data of Table III also show the effect of increasing amounts of ammonia in decreasing the $i\text{C}_4/n\text{C}_4$ ratio. It is thus apparent that the main effect of ammonia is to reduce the acidic cracking properties of the melt by neutralizing the Friedel Crafts acids.

Friedel Crafts acids in the case of extract hydrocracking can be generated by formation of several different zinc chloride complexes such as with phenolic groups in the extract, with water and with HCl formed by reaction (1).

It is also noted in Table III, from the catalyst analyses given, that as discussed above a very high percentage of the original nitrogen and sulfur in the feed extract is retained by the catalyst when the extract conversion is high.

Five-Stage Run

The above discussion indicates that if the NH_3 accumulates mostly as NH_4Cl relatively little deactivation of the catalyst occurs. This would be attractive from the practical point of view since it is desirable to reduce the melt circulation rate between regeneration and hydrocracking.

A five-stage run was carried out to demonstrate this. After each stage, the autoclave was cooled to 250°C and depressurized with removal of volatile liquid products and gas. After further cooling, fresh zinc chloride and extract were added (in a weight ratio of 0.23/1) to the catalyst and high-boiling liquid remaining in the autoclave from the previous stage. The autoclave was repressurized with hydrogen and heated back to the operating conditions of 750°F and 3000 psig.

The results after a single-stage are compared with the cumulative results of the five-stage run in Table IV. It is noted that the cumulative results of the five stages are very nearly equivalent to that of the first stage. However, a favorable net reduction in catalyst/extract ratio from 1 to 0.38 is achieved by this technique.

The composition of the catalyst after stages 1 and 5 is also shown in Table IV. It is seen that 82 percent of the nitrogen and 95 percent of the sulfur in the feed accumulate in the melt. The NH_3 is present mostly as NH_4Cl which explains the relatively small loss in catalyst activity.

A chlorine balance around the five-stage run indicates that 85 percent of the HCl released by reaction (1) was retained in the melt. The nature of HCl loss is not clear, however, as none could be found in the off-gas.

Kinetics of the Hydrocracking Process

The maximum extract conversion achieved in 60 minutes residence time in the experiments reported above was 91 percent. It, of course, is desirable to achieve substantially complete conversion. In order to accomplish this it is first of all necessary to substantially reduce the yield of MEK-Insolubles. Secondly, it is necessary to hydrocrack the +400°C MEK-Solubles to distillate oils.

Another characteristic of the previous experiments is that although the total hot pressure was maintained constant, the partial pressure of hydrogen decreased with time due to accumulation of gas and volatile reaction products. The hydrogen pressure is the most important variable in controlling the MEK-Insoluble yield. A series of runs were therefore carried out wherein the hydrogen pressure was maintained constant using a palladium probe to indicate hydrogen partial pressure.

The results of two series of runs at various times carried out at 750°F wherein the hydrogen partial pressures were maintained constant at 2500 psi and 3500 psi, respectively, are shown in Figure 7.

The MEK-Insoluble yield rapidly falls to a nearly constant value after 15 to 30 minutes time after which very little further reduction occurs. The final yield is, of course, lower at the higher hydrogen pressure, i.e., 1.5 percent vs. 3.5 percent.

The rate of total conversion decreases rapidly with time and becomes very slow after one hour. Even after three hours the total conversion only reaches 92.1 percent at 3500 psi and is slightly lower at 2500 psi H₂ pressure.

The cause of the difficulty is shown in Figure 8 where the reaction rate for conversion of the +400°C MEK-Solubles is plotted as a first order reaction, i.e.,

$$k(t - 15) = \ln C_0/C_t$$

where C₀ and C_t are the weight percent MEK-Solubles present after 15 minutes and time "t", respectively.

It is seen that the initial rate follows the first order rate law but that the rate falls off rapidly as high conversions are reached. The first order rate increases about 20 percent in going from 2500 to 3500 psi, i.e., less than proportional to increase in pressure.

The higher pressure does not likewise prevent the decrease in rate at high conversions. As a matter of fact at both pressure levels the same yield of MEK-Soluble residue, i.e., 6.2 wt. % remains after three hours.

The decrease in reaction rate is due to formation of a refractory residue and not to decrease in catalytic activity of the melt. That this is so is obvious from the fact that over 95 percent of N and S catalyst poisons have accumulated in the melt after one hour residence time, i.e., long before the rate starts to decrease. It was also confirmed by recovery and separate hydrocracking of the MEK-Soluble residue.

It is clear that to obtain higher conversions a staged hydrogenation system with progressive increase in temperature would be required.

Effect of Feedstock - Direct Hydrogenation of Coal

The use of molten zinc chloride hydrocracking catalyst is not limited, of course, to coal extract but may be applied to a wide range of feedstocks varying from coal itself to middle boiling range petroleum distillates.

A comparison of results with several other coal derived feedstocks is given in Table V. Ireland Mine coal, a Pittsburgh Seam coal from Northern West Virginia, is the coal used for production of the standard extract used in most of this work. It was necessary to use a high ratio of catalyst to coal in this case in order to have sufficient volume of liquid present to produce a handleable coal slurry. As stated above, the use of a catalyst ratio above 1 with extract only increases the conversion slightly but has a relatively marked effect on gas yield. Thus, allowing for the difference in quantity of catalyst used, it is seen that coal and extract behave with remarkable similarity.

Results are also shown for another extract, i.e., "Spencer" extract. This extract was procured from the Spencer Chemical Co., and was prepared by extraction of a West Kentucky No. 11 coal under a pressure of 1000 psig of hydrogen at about 425°C. The depth of extraction was reported by Spencer Chemical to have been over 90%. Inspections of the extract are given in Table I.

Comparison should be made with the 750°F standard extract results of Table IV (Stage 1). Again a remarkable similarity is noted although the yield of middle range distillate is higher and the overall conversion slightly lower.

Results with a higher quality feedstock, i.e., benzene-soluble component of standard extract, are also shown in Table V. In this case a notable improvement in results is noted. The conversion is substantially increased while the yield of MEK-Insoluble residue is substantially decreased.

Gasoline Composition

The gasoline produced by the zinc chloride process contains a high proportion of branched paraffins and a substantial amount of aromatics. The aromatic content of the gasoline varies with conditions used from about 20 to 50 vol. percent. High aromatic contents are obtained in operations at the higher temperatures around 800°F and with catalyst/extract ratios below one.

A sample of gasoline from a large number of autoclave runs at different conditions was composited for a micro octane number test with results shown in Table VI along with inspections of the gasoline. The gasoline sample tested had substantially all the C₄'s and C₆'s removed but in spite of this had a clear research octane of 89. It is clear that a motor gasoline with the appropriate C₄'s and C₅'s added for volatility would have a clear octane number of well over 90.

Another sample of gasoline was obtained by running a number repetitive autoclave runs at Stage 1 conditions shown in Table IV. A more complete analysis of this gasoline is given in Table VI along with a breakdown into individual components.

The ratio of branched-to-normal paraffins is clearly quite large in the C₅ and C₆ fractions.

Potential Commercial Considerations

It is premature to discuss in detail the potential commercial application of the zinc chloride hydrocracking process. Data are required both on continuous hydrocracking and continuous melt regeneration systems. Work is presently in progress on both of these subjects and will be reported in future papers. Some aspects of the regeneration process is discussed in a subsequent paper.

Corrosion control is one of the important aspects of a potential commercial process. Weight loss data over the duration of the autoclave program indicate that the average penetration rate with 316 stainless is less than 80 mpy. Separate

corrosion tests, however, have indicated that pitting may be a problem with 316 stainless when substantial quantities of NH_4Cl are allowed to build up in the melt. In this case more expensive alloys such as Hastelloy B or Inconel 625 may be required.

The formation of NH_4Cl can be eliminated by addition of zinc oxide acceptor. Corrosion test work in this case indicates that 316 stainless may be a satisfactory alloy, i.e., penetration rates below 5 mpy were observed with test specimens.

Therefore, from the corrosion standpoint the zinc-oxide acceptor system is preferred. The disadvantage is the lower catalyst activity for a given nitrogen level. The inhibiting effect of ZnO can be minimized by maintaining at all times a very low concentration of zinc oxide in the hydrocracking zone and by providing for a staged increase in temperature to over 800°F to partially compensate for decrease in catalyst activity by accumulation of NH_3 in the melt. Figure 9 illustrates schematically a continuous operation using the above principles. It should be noted that the zinc chloride melt is miscible with extract, as it was with pyrene.⁽¹⁰⁾

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TABLE I Analysis of Feedstocks

Feedstock	Ireland	"Standard"	"Spencer"	Benzene Solubles
	Mine Coal	Extract	Extract	
	<u>MF Basis</u>			
Volatile Matter	40.32			
Fixed Carbon	46.66			
FeS	0.08			
FeS ₂	4.19			
Other Ash	10.15			
	<u>MAF Basis</u>			
H	5.73	6.14	5.03	7.04
C	81.90	83.73	87.62	85.30
N	1.58	1.46	1.49	.94
O	8.61	6.87	4.75	5.10
Organic S	2.18	1.80	1.11	1.62
<u>Solvent Fractionation</u>				
Benzene Insolubles		46.9	37.2	.5
Asphaltenes		37.2	31.2	59.6
Oil		15.9	31.5	39.0

TABLE II Comparison of Catalyst Activity at Low Concentration Levels - 1 Hr. Residence Time

Temperature, °F	← 800 →		
	4200	4200	3000
Total Hot Pressure			
Catalyst	Nickel Molybdate on Al ₂ O ₃	ZnCl ₂	SnCl ₂
Catalyst/Extract, Wt. Ratio	.025	.02	.01
<u>Yields, Wt. % Feed</u>			
C ₁ -C ₃	5.0	5.1	4.1
C ₄) 14.9	1.0	1.8
C ₅ x 200°C		14.7	13.0
200 x 400°C	14.5	19.8	24.6
MEK-Soluble +400°C Residue	60.3	52.9	53.5
MEK-Insoluble +400°C Residue	0.6	3.0	0.1
Other (NH ₃ , H ₂ S, H ₂ O, etc.)	7.3	7.6	6.7
Total	102.6	104.1	103.8
H ₂ Consumption, Wt. % Feed	2.55	4.13	3.71
Conversion, Wt. % Feed	39.0	44.1	46.5
(C ₁ -C ₃) x 100/Conversion	12.8	11.5	8.8

TABLE III

Activity of Zinc Chloride Catalyst as Affected

by NH₃ Addition

Temperature = 800°F, Total Pressure = 4200 psig

ZnCl₂/Extract Wt. Ratio = 1.0, Time = 60 mins.

NH ₃ /ZnCl ₂ , Mole Ratio	0	0.091	1.0	2.0
<u>Yields, Wt. % MAF Feed</u>				
CH ₄	1.8	1.5	1.6	1.8
C ₂ H ₆	2.6	1.7	1.2	1.4
C ₃ H ₈	8.6	3.0	1.2	1.2
i C ₄ H ₁₀	9.6	2.5	0.4	0.1
n C ₄ H ₁₀	1.6	0.5	0.5	0.5
(NH ₃ +H ₂ S+H ₂ O+CO+CO ₂)	7.4	7.4	5.5	2.3
C ₅ x 200°C Dist.	60.4	68.2	15.8	10.3
200 x 400°C Dist.	3.1	11.4	19.1	9.5
+400°C MEK-Soluble Residue	6.3	6.2	54.5	54.1
+400°C MEK-Insoluble Residue	3.9	2.6	2.4	20.3
N to Catalyst	1.3	1.3	} 1.6	} 1.4
S " "	1.8	1.4		
H " "	0.3	0.3		
Total	108.7	108.0	103.8	102.9
Conversion, Wt. % MAF Feed	89.8	91.2	43.2	25.6
H ₂ Consumed, Wt. % MAF Feed	8.7	8.0	3.8	2.9
(C ₁ -C ₃) x 100/Conversion	14.5	6.8	9.3	17.1

TABLE IV

Results of 5-Stage Run

Temperature = 750°F, Total Hot Pressure = 3000 psig

Residence Time/Stage = 60 mins.

Stage No.		<u>1</u>	<u>2 thru 5</u>	<u>Cumulative</u>
Wt. Extract Feed Per Stage/gms		50	50	250
Wt. ZnCl ₂ Feed Per Stage/gms		50	11.4	95.6
Cumulative ZnCl ₂ /Extract, Wt. Ratio		1	--	0.383
<u>Melt Composition, Mole %</u>	<u>Feed</u>	<u>After Stage 1</u>		<u>After Stage 5</u>
	ZnCl ₂	81.7		48.5
	ZnO	--		--
	ZnCl ₂ ·NH ₃	2.3		4.4
	ZnCl ₂ ·NH ₄ Cl	8.9		27.4
	ZnS	7.1		19.7
	<u>100.0</u>	<u>100.0</u>		<u>100.0</u>
<u>Yields, Wt. % Total Extract Feed</u>				
	C ₁ -C ₃	6.3		6.3
	i C ₄ H ₁₀	3.3		3.2
	n C ₄ H ₁₀	0.4		0.6
	CO	0.1		0.2
	H ₂ O	7.3		5.8
	C ₅ x 200°C Dist.	59.0		56.0
	200 x 400°C Dist.	9.6		14.3
	+400°C MEK-Soluble Residue	11.9		12.9
	+400°C MEK-Insoluble Residue	6.4		4.5
	H to Catalyst	0.3		0.3
	N " "	1.1		1.2
	S " "	1.6		1.7
Total		107.3		107.0
Conversion, Wt. % MAF Feed		81.8		82.6
H ₂ Consumed, Wt. % MAF Feed		7.3		7.0
(C ₁ -C ₃) x 100/Conversion		7.7		7.6

TABLE V

Comparison of Feedstocks in Hydrocracking
With Molten Zinc Chloride Catalyst

Residence Time = 60 min.

Feedstock	Ireland Mine Coal	Standard Extract	Spencer Extract	Benzene Solubles from Standard Extract
Temperature, °F	725	725	750	750
ZnCl ₂ MAF Feed (Wt. Ratio)	3.5	1.0	1.0	1.0
Total Pressure, psig	2000	2000	3000	3000
<u>Yields, Wt. % MAF Feed</u>				
CH ₄	0.9	0.6	0.6	.6
C ₂ H ₆	2.3	1.2	0.8	1.2
C ₃ H ₈	7.5	1.7	2.1	5.8
i C ₄ H ₁₀	7.8	1.2	2.1	7.3
n C ₄ H ₁₀	1.3	0.1	0.3	1.0
(NH ₃ +H ₂ S+CO+CO ₂ +H ₂ O)	6.7	6.9	6.8	7.0
C ₅ x 200°C Dist.	48.2	49.5	50.4	66.2
200 x 400°C Dist.	2.9	9.4	17.9	6.2
+400°C MEK-Soluble Residue	15.0	17.0	17.9	7.7
+400°C MEK-Insoluble Residue	10.9	14.8	5.7	1.2
N+S+H to Catalyst	5.2	3.5	2.3	3.1
Total	108.7	105.9	106.9	107.3
Conversion, Wt. % MAF Feed	74.2	68.1	76.4	91.1
H ₂ Consumption, Wt. % MAF Feed	8.7	5.9	6.9	7.3
(C ₁ -C ₃) x 100/Conversion	14.3	5.1	4.6	8.3

TABLE VI

Analyses of Product Gasoline

Description	<u>C₅-200°C Gasoline</u>	<u>C₆-190°C Gasoline</u>
<u>FIA, Vol. %⁽¹⁾</u>		
Aromatics	25.5	30.9
Saturates	74.5	69.1
Olefins	0.0	0.0
Naphthenes	Not Determined	31.7 ⁽²⁾
Research, Clear Octane No.	" "	89
<u>Elemental Analytical, Wt. %</u>		
H	13.42	12.93
C	86.22	87.00
N	0.0	.04
O	.34	.03
S	.02	0.0
<u>Partial Component Breakdown, Vol. %</u>		
<u>Saturates</u>		
i-Pentane	13.4	
n-Pentane	1.2	
Cyclopentane	.8	
2,3-Dimethylbutane	1.1	
2-Methylpentane	4.4	
3-Methylpentane	3.0	
n-Hexane	.5	
Cyclohexane	.6	
Methylcyclopentane	9.3	
<u>Aromatics</u>		
Benzene	2.0	
Toluene	5.9	
Ethyl Benzene	2.4	
Xylenes	3.9	
Cumene	1.1	
n-Propyl Benzene	.5	

(1) Fluorescent Indicator Analysis, A.S.T.M. Method D-1319-61T.

(2) The total saturates are 31.7% naphthenic and 37.4% paraffinic as determined by A.S.T.M. Method D-2159.

Figure 1

EFFECT OF FEED CATALYST-EXTRACT RATIO ON TOTAL CONVERSION AND CONVERSION TO GASOLINE

800°F - 4200 psi Total Pressure.
- 60 min. R.T.

▲ Molten ZnCl₂ Catalyst.
○ Nickel Molybdate Hydrofining Catalyst.

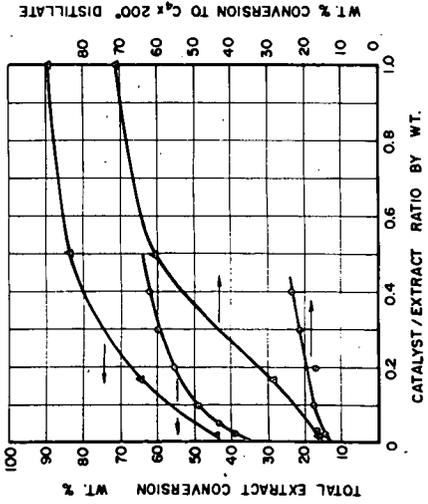


Figure 2

EFFECT OF CATALYST-EXTRACT RATIO ON C₄-C₄ RATIO AND SELECTIVITY

800°F - 4200 psi Total Pressure.
- 60 min. R.T.

▲ Molten ZnCl₂ Catalyst.
○ Nickel Molybdate Hydrofining Catalyst.

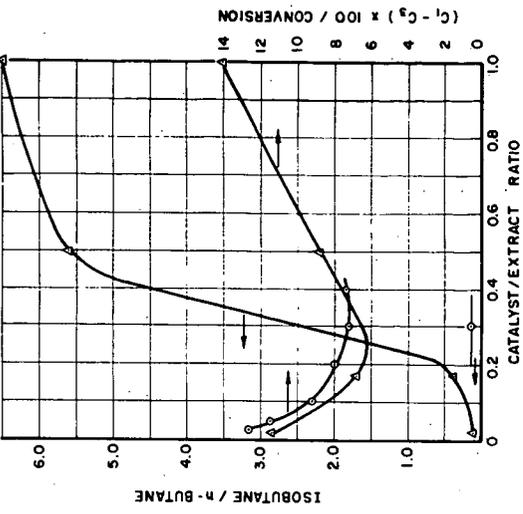


Figure 4
EXTRACT CONVERSION
VS
TEMPERATURE & PRESSURE

Zn Cl₂ / Extract = 1.0
 Time = 1 Hour

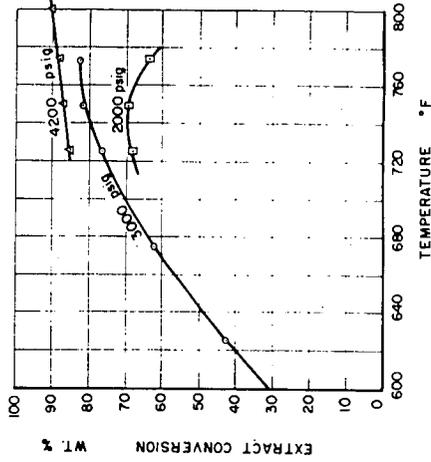


Figure 3
EFFECT OF RESIDENCE TIME
ON TOTAL CONVERSION

Δ Zn Cl₂ / Extract = 1
 ○ Nickel Molybdate / Extract = 0.3

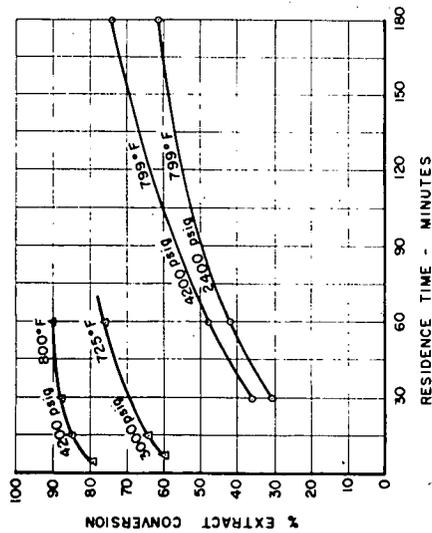


Figure 6
**EFFECT OF NH₃ & NH₄Cl ON
 CONVERSION & SELECTIVITY**

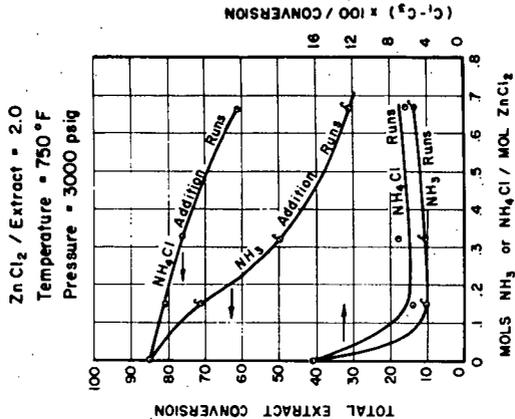


Figure 5
**GASOLINE YIELD & SELECTIVITY
 VS
 TEMPERATURE**

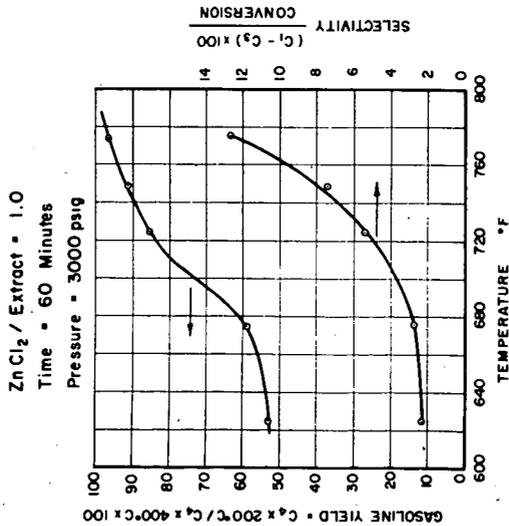


Figure 7
YIELDS vs TIME IN CONSTANT
HYDROGEN PRESSURE RUNS
AT 750° F

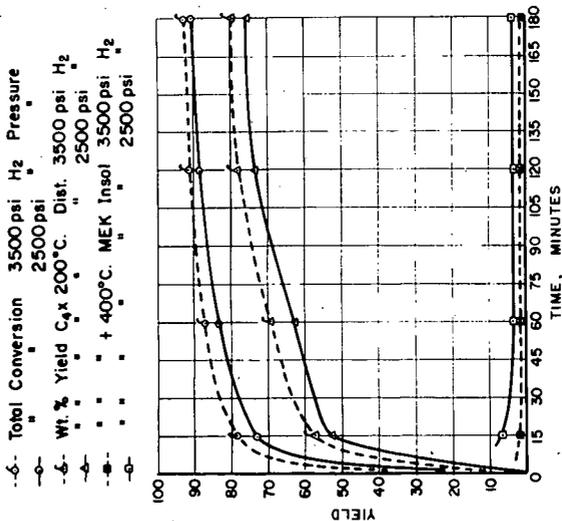


Figure 8
RATE OF HYDROCRACKING OF
+400°C MEK SOLUBLE RESIDUE

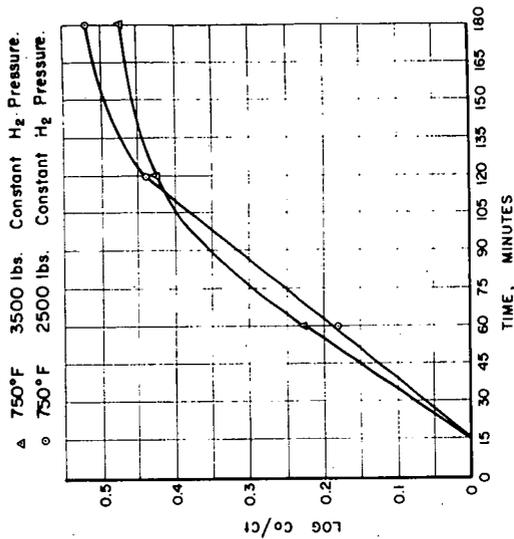
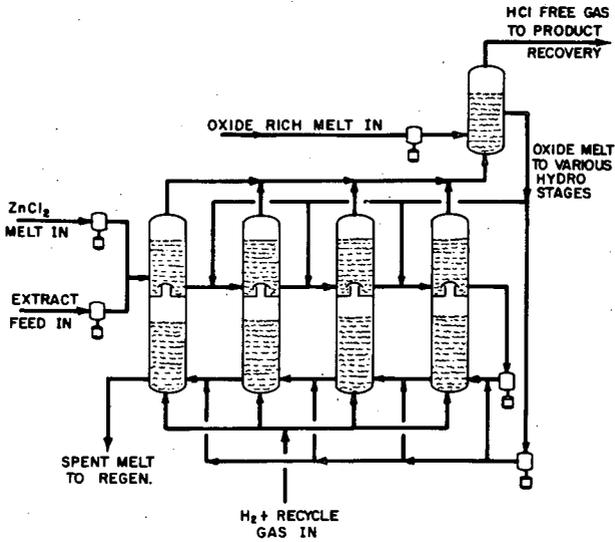


Figure 9

**SCHEMATIC HYDRO SYSTEM WITH MASSIVE
ZINC CHLORIDE MELT CATALYST
ZINC OXIDE ACCEPTOR SYSTEM**



REGENERATION OF ZINC HALIDE CATALYSTS USED IN HYDROCRACKING OF COAL EXTRACT

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Research Division
CONSOLIDATION COAL COMPANY
Library, Pennsylvania

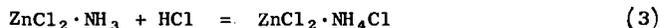
INTRODUCTION

The application of molten zinc chloride catalysis to the hydrocracking of poly-nuclear hydrocarbons, coal extract and coal was discussed in two previous papers.^(a,b) The zinc chloride, however, is not a catalyst in the chemical sense since it is partially destroyed by reaction with the N and S impurities in the hydrocracker feed. When coal itself is used further complications arise due to reactions with some of the inorganic components in the coal ash.

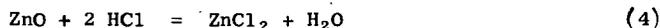
A commercial process utilizing molten zinc chloride catalysis must provide a viable scheme for regeneration of the catalyst.

Two schemes for using the catalyst were discussed in a previous paper, i.e., with and without the concomitant addition of zinc oxide acceptor.

The following reactions occur when no acceptor is added:



The addition of zinc oxide acceptor eliminates reaction (3) and introduces a new reaction



The present paper will discuss only the regeneration of the catalyst for the non-acceptor case. The acceptor case will be discussed in a separate paper.

The melt leaving the hydrocracker thus, in general, will contain in addition to ZnCl_2 the following compounds: ZnS , $\text{ZnCl}_2 \cdot \text{NH}_3$ and $\text{ZnCl}_2 \cdot \text{NH}_4\text{Cl}$. The addition compounds between zinc chloride and NH_3 and NH_4Cl are written as the 1/1 adducts not because they necessarily exist as such in the melt but for convenience of discussion. The ratio of the NH_4Cl to the NH_3 adducts is dependent on the ratio of N to S in the feed. Where the moles of sulfur in the hydrocracker feed is equal to or greater than one-half the moles of nitrogen, substantially all of the NH_3 will be present as the NH_4Cl double salt.

Regeneration of the melt comprises removal of the bulk of the sulfur and nitrogen and return of the melt as relatively pure zinc chloride.

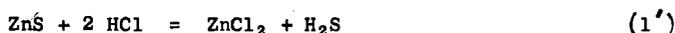
From the economic point of view it would be desirable to recover the sulfur in the form of elemental sulfur and the nitrogen as ammonia such that credits for these materials would partially defray the regeneration cost.

In addition to the inorganic impurities in the spent melt, the melt contains organic impurities which cannot be distilled out of the melt. The organic residue itself can be

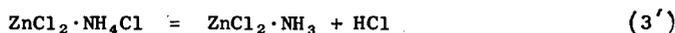
divided into two parts, one soluble in MEK and the other insoluble. The first part is largely convertible to distillate oil on recycle while the latter is mostly unconvertible and can be regarded as semi-coke. The regeneration process thus must in addition remove the organic residue from the melt before it can be recycled, coked or otherwise processed.

The reactions which are involved for specific components of the spent melt are listed below. Most of these reactions involve simple reversal of the reactions by which they were formed, i.e., reactions (1), (2) and (3) above. Where this is the case the number of the reaction is primed.

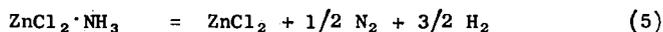
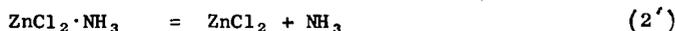
Regeneration of Zinc Sulfide



Regeneration of Ammonium Chloride-Double Salt



Regeneration of $\text{ZnCl}_2 \cdot \text{NH}_3$



It is the purpose of this paper to present thermodynamic and other data bearing on the feasibility of the particular regeneration scheme shown. The data on the individual process steps involved are presented. The integration of the individual process steps into the overall scheme is also given.

EXPERIMENTAL

Equipment and procedures for hydrocracking of coal extract with zinc chloride catalyst have been given previously.⁽⁸⁾

Figure 1 shows the apparatus used to determine the equilibria in the decomposition of the zinc chloride-ammonium chloride double salt. A flow system was used with nitrogen passing slowly through a molten bed of $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$ and the exit gas being analyzed for HCl. A number of points taken over a period resulted in curves of HCl partial pressure versus the extent of NH_4Cl decomposition.

The zinc chloride and ammonium chloride used were Fisher Scientific Co. Certified Reagents. The zinc chloride was 98 percent pure, the impurities being water and zinc oxide. This material was purified at the start of each run by heating to 425°C in a flow of purified nitrogen to remove water, and then passing anhydrous HCl through it for two hours to convert ZnO to ZnCl_2 . This was followed by a nitrogen purge of 12 to 36 hours to remove excess HCl from the melt. The nitrogen used was purified by passage through hot copper, Ascarite, and magnesium perchlorate to remove traces of oxygen, carbon dioxide and water.

After purifying the zinc chloride, the reactor temperature was lowered to 343°C to minimize the possible loss of HCl when adding NH_4Cl through a long stem funnel inserted in the stirrer annulus (3 seconds required). The reactor was then brought to the desired temperature with a low flow of nitrogen (1 ml/min). The desired temperature was controlled to $\pm 2^\circ\text{C}$ and the nitrogen rate raised to the operating flow of 4.7 ± 0.2 cc/min (STP). The nitrogen gas reaches equilibrium HCl content in passing through the molten bed as shown by identical results at flows between 4.7 and 12 cc/min and stirring rates from the 3100 rpm used down to as low as 1500 rpm. The gas from the reactor passes through a caustic trap and is collected in a bottle by water displacement. Two recovery trains used alternately allow continuous collection.

The 0.1 or 1.0 N caustic used in the traps is titrated after use with 0.1 or 1.0 N HCl using methyl red indicator. Caustic traps are used even during lineout periods so the amount of NH_4Cl remaining in the melt can be accurately calculated.

Collection of the effluent nitrogen in bottles allowed accurate measurement of flow rates using weight of water remaining after adjustment of the gas to atmospheric pressure.

When most of the NH_4Cl had decomposed, pressure of NH_3 over the bed became appreciable, combining with HCl on cooling to form solid NH_4Cl in the glass wool trap. Analyses of these solids confirmed that they were mostly NH_4Cl . At 427°C , a small amount of ZnCl_2 was also found in the glass wool trap. The partial pressures of HCl calculated by caustic titration were corrected by adding the additional HCl tied up as solid NH_4Cl in the solids trap.

Equilibrium data for zinc sulfide regeneration (Reaction (1'), Table III) were determined in a static glass system. After adding ZnS , the vessel was evacuated and brought to temperature under vacuum. The vacuum was then shut off and aqueous HCl added in increments. After each increment, the slurry was stirred and allowed to reach steady state before the pressure was measured. For purposes of the rough figures reported in Table III, the H_2S pressure was taken as the total pressure minus the vapor pressure of water at the temperature used. The normality of the acid was determined by titration after completion of the run.

The phase separation studies reported in Table II were conducted in the same type of rocking autoclave used for hydrocracking tests.^(8a) The synthetic spent melt, whose composition is given in Table IIA, was charged to the autoclave along with the desired amount of water or in the final test, with water plus dimethylnaphthalene (Table IIB). After flushing the air with nitrogen, the unit was heated to temperature and rocked for an additional 30 minutes. The autoclave was then tilted vertically and allowed to stand for one hour before bleeding off the contents through the bottom. The products were collected in about 8 increments which were then usually combined as "organic" and "aqueous" phases. The aqueous phase was washed with benzene to remove organics before distilling off the water. The organic phase was likewise distilled to $+400^\circ\text{C}$ end point to remove any light material before analysis. Methods of analysis for the zinc salts, NH_3 , and NH_4Cl were given previously.^(8a)

RESULTS AND DISCUSSION

1. Separation of Organic Residue from Spent Melt

No substantial separation of phases was ever observed for mixtures of zinc chloride melt with high boiling organic materials such as extract, pyrene or hydrocracking residues. A number of different conditions were tried using separation times of up to one hour, with negative results.

The results of one such experiment are summarized in Table I. In this experiment extract was hydrocracked with zinc chloride melt at 750°F and 3000 psig. When the run was completed the autoclave was placed in a horizontal and then a vertical position for 15 minutes each while maintaining temperature and pressure. A number of samples were successively withdrawn over an additional 15 minute period and analyzed as shown.

It is seen that the amount of ZnCl_2 and organic residue remained reasonably constant over the first six samples indicating no phase separation. The hydrocarbon distillate showed considerable fluctuation from sample to sample but no definite trend is discernable. The bulk of the distillate was withdrawn with the bulk of the gas in the last sample. It is likely that most of the distillate was actually in the vapor phase as the temperature used was above the critical temperature of most gasoline components.

It therefore does not appear possible to effect a phase separation between the high-boiling organics and the catalyst melt and this must be taken account of in any regeneration scheme. The high-boiling residue still contains substantial quantities of N, O and S which hetero atoms may complex with the zinc chloride catalyst to form a true solution. On the other hand, polynuclear hydrocarbons such as pyrene which do not contain hetero atoms also do not separate.^(8a) It thus is not ruled out that one is dealing with a relatively stable emulsion.

It is noted likewise that no concentration of ZnS by settling is apparent from Table I. Separate experiments were conducted in which ZnCl₂ melts were mixed with powdered ZnS and allowed to stand. Again, no phase separation was observed. Since the solubility of ZnS in molten ZnCl₂ is known to be small,⁽³⁾ this is clearly a case of a stable dispersion rather than solution.

Recovery of the organic residue therefore requires addition of another component which will cause phase separation to take place. If solution of unconverted extract is due to complex formation with zinc chloride, it would be logical to assume that phase separation could be effected by addition of agents which themselves complex with zinc chloride such as H₂O, CH₃OH, NH₃ and NH₄Cl. All of these materials have been found in preliminary experiments to be capable of effecting the desired phase separation. At the time of this writing, water addition has been most thoroughly investigated and only some of these data at 200 and 250°C are presented. Composition of the separated phases after water addition are given in Table IIA.

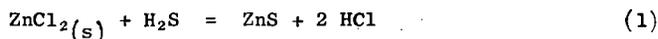
The feed melt composition used in this study was a simulated spent melt and had the composition given in the bottom of Table IIA. Extract was used in place of hydro residue due to shortage of the latter material. Since separation of extract from spent melt is, if anything, more difficult, the results are adequately conservative.

Adequate separation of the extract from the zinc chloride phase takes place at water/melt ratios of 0.3 or greater. The sharpness of separation of the zinc chloride from the organic phase leaves something to be desired, however, especially at low water/melt ratios. The difficulty is due to physical occlusion of aqueous zinc chloride in organic phase. The organic phase is a highly viscous mass that does not flow readily, thus making a sharp separation difficult. The high viscosity is due in part to the inherent high viscosity of the extract and secondly due to dispersion of the zinc sulfide in the organic phase. The zinc sulfide was surprisingly in all cases nearly quantitatively transferred to the organic phase.

The addition of aromatic solvents was investigated in order to improve the sharpness of separation. One such experiment is shown in Table IIB. The added solvent made it possible to withdraw the organic phase as a fluid liquid due to the effect of the solvent in cutting the viscosity. The organic phase was relatively free of inorganic components. In contrast to the previous case most of the ZnS was found in the aqueous phase. This points to physical trapping by the viscous extract as the principle reason for transferral of the ZnS to the organic phase in the previous instance.

2. Regeneration of Zinc Sulfide via Reversal of Reaction (1)

The equilibrium in reaction (1) has been measured by Britzke and Kapustinsky⁽²⁾ down to the melting point of ZnCl₂. Their data were then extrapolated below the melting point using the heat of reaction



$$\Delta H = +16,700 \text{ cal/mole}$$

as determined from the thermochemical data given in Bichowsky and Rossini.⁽¹⁾ The result is

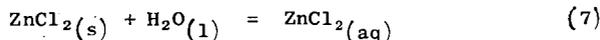
$$\log K_p = \frac{-3360}{T} + 7.62 \quad (6)$$

The equilibrium becomes less favorable with decreasing temperature such that reversal of the reaction becomes feasible at temperatures of the order of 200°C or less, i.e., $K_p = 1.0$ at 207°C. For example, at 100°C

$$K_p = P_{\text{HCl}}^2 / P_{\text{H}_2\text{S}} = 6.46 \times 10^{-3}$$

Thus, if reversal of the reaction is effected with 0.1 atmosphere of HCl, the ratio $P_{\text{H}_2\text{S}} / P_{\text{HCl}} = 15.5$ at 100°C.

In actual practice, reversal of reaction (1) can only be effected after addition of sufficient water to maintain a liquid phase. The equilibrium for reversal will now even be more favorable since there is a negative free energy change for the reaction



The effect of using aqueous solutions in facilitating the reversal of reaction (1) is illustrated by some equilibrium data measured by us in dilute aqueous solutions as shown in Table III. The equilibrium is now much more favorable and reversal of reaction (1) with aqueous solution of zinc chloride is to be regarded as a feasible process. Experiments were conducted wherein actual spent melts from hydrocracking of extract were treated with aqueous hydrochloric acid. Rapid evolution of H_2S was noted.

3. Decomposition of Zinc Chloride-Ammonium Chloride Double Salt

The reaction in question is the reversal of reaction (3) which not only supplies the HCl required for regeneration of zinc chloride from zinc sulfide, but eliminates HCl from the melt prior to recovery of the NH_3 . Equilibrium measurements were accordingly made over the range 340-450°C and for initial concentrations of NH_4Cl in the range of 10 to 20 mole percent. The partial pressure of HCl in equilibrium with the melt as a function of percent NH_4Cl decomposed is shown in the semi-log plot of Figure 2.

The smoothed data from Figure 2 are replotted to define a "pseudo" equilibrium constant K.

$$P_{\text{HCl}} = K \frac{(1 - \alpha)}{\alpha} \quad (8)$$

where α is the fraction of NH_4Cl decomposed. Adequate straight lines are obtained (Fig. 3) although slight tailing off is noted in some cases at high conversion levels. This may be due to experimental error as a result of slight losses of NH_3 from the melt. The NH_3 was collected and analyzed as NH_4Cl and corrections made for its loss. However, if the measurements of volatilized NH_3 were slightly low, it would produce the tailing off observed. The values of K are considerably greater for the 10 mole percent NH_4Cl series than for the 20 mole percent NH_4Cl series. No adequate explanation for this phenomenon can be advanced at this time.

A semi-log plot of the HCl pressure versus the reciprocal of the absolute temperature at constant percent NH_4Cl decomposition is given in Figure 4. The slopes of the lines correspond to the heat of decomposition,

$$\Delta H = 21,000 \pm 600 \text{ cal/mole}$$

It is now possible to express values of K as a function of the temperature in degrees Kelvin by the expressions

$$\log K = \frac{-4590}{T} + B \quad (9)$$

where $B = 6.32$ and 6.14 when the initial NH_4Cl concentrations are 10 and 20 mole percent, respectively, and the HCl partial pressure in the expression for K is given in atmospheres.

In practice, HCl would be removed from the melt by stripping with hot gas in a countercurrent tower. The HCl concentration in the gas as a function of that in the melt at any point in such a tower is given by the simple material balance relationship

$$P_{\text{HCl}} = \frac{(\Delta - \Delta_f)}{(\Delta - \Delta_f + r)} \cdot \pi \quad (10)$$

The equilibrium pressure of HCl over the melt is likewise given by

$$P_{\text{HCl}}^{\text{eq.}} = K \left(\frac{\Delta}{1 - \Delta} \right) \quad (11)$$

where Δ = Mole fraction of total NH_3 in melt combined with HCl .

Δ_f = Value of Δ in melt leaving tower.

π = Total pressure in atmospheres.

r = Moles of stripping gas/mole of $\text{NH}_3 + \text{NH}_4\text{Cl}$ in melt.

It is clear that in order to have a net driving force for HCl evolution $P_{\text{HCl}}^{\text{eq.}} > P_{\text{HCl}}$ everywhere in the tower. Consider the case, for simplicity, where the melt is nearly quantitatively stripped of HCl , i.e., $\Delta_f \cong 0$. The above condition is satisfied if

$$\left(\frac{dP_{\text{HCl}}}{d\Delta} \right)_{\Delta=0} \leq \left(\frac{dP_{\text{HCl}}^{\text{eq.}}}{d\Delta} \right)_{\Delta=0} \quad (12)$$

Differentiating equations (10) and (11), the inequality may be written,

$$\pi/r \leq K \quad (13)$$

For example, if the temperature at the melt outlet is 460°C , and the mole fraction of $\text{NH}_3 + \text{NH}_4\text{Cl}$ in the melt is 0.20, then $\pi/r \cong .73$.

A net driving force for HCl evolution can still be maintained in such a tower, even if, as will normally be the case, the temperature decreases from bottom to top. The more general inequality can be obtained if the differentiation of equations (10) and (11) above is performed with the equilibrium constant K as function of Δ and therefore also of temperature (i.e., Δ is considered to be a function of temperature). The result is, again for case where $\Delta_f \cong 0$,

$$\frac{K_0}{(1 + \Delta/r)^2} \leq \left(\frac{\Delta}{1 - \Delta} \right) \frac{dK}{d\Delta} + K \left(\frac{1}{1 - \Delta} \right)^2 \quad (14)$$

where K_0 is the value of K at melt outlet, i.e., where $\Delta = 0$. Equation (14) in combination with equation (9) thus can be employed to define the maximum allowable rate of decrease in temperature with respect to Δ in the tower and thus is useful for design purposes.

4. Decomposition of Zinc Chloride-Ammonia Adduct

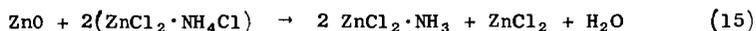
The final regeneration of the spent melt requires that a major fraction of the ammonia be removed. This can be done in principle by thermal decomposition of the adduct which amounts to a reversal of reaction (2). This would be attractive since recovery of NH_3 would bring substantial by-product credits.

The design of such an NH_3 adduct decomposition tower requires equilibrium data which give the partial pressure of ammonia over the melt as a function of its ammonia content and temperature. Equilibrium measurements in this system have been made by Kurilov,⁽⁶⁾ Koeneman⁽⁴⁾ and Krasnov.⁽⁵⁾ The above authors in the order named measured the ammonia pressures at successively increasing temperatures and decreasing ammonia content.

The data of these authors are summarized in graphical form in Figure 5. A log-log plot is used to permit some extrapolation outside the range of the data. No experimental points are available below 3.4 wt. percent of NH_3 .

The ammonia content of the melt sent to the ammonia decomposer in practice will vary between 1.5 and 5.0 wt. % depending upon the melt circulation rate used. It is clear, however, from the data of Figure 5 that it will be very difficult to achieve very low NH_3 concentrations, i.e., below 1% in the regenerated melt unless temperatures well above those investigated are used.

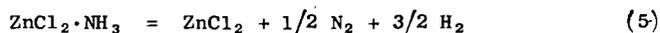
It is not necessary, however, to reduce the NH_3 content of the regenerated melt to zero. It has been found, for example, that the reaction



goes quantitatively to the right at temperatures in the neighborhood of 400°C. The melt leaving the NH_4Cl decomposer will therefore be free of zinc oxide. This is in contrast to the feed melt to the hydrocracking runs described in a previous paper^(8b) which contained 2.8 mole % of ZnO . Equivalent hydrocracking results will therefore be obtained with a regenerated melt containing .056 moles NH_3 /mole ZnCl_2 (0.7 wt. % NH_3) to those reported experimentally which contained .056 moles NH_4Cl /mole ZnCl_2 . The above result follows since reaction (15) proceeds in the melt used in the experimental work to produce an identical melt composition in both cases. The activity of the melt in this case [cf. Figure 6 of previous paper^(8b)] is only negligibly less than that of a melt containing no NH_4Cl .

The ammonia decomposition equilibrium at lower NH_3 concentrations and higher temperatures is presently being investigated in the Consolidation Coal Co. laboratories but no data are available as yet.

One interesting observation has been made, however, that the reaction



is readily catalyzed by oxidized metal surfaces. Thus, it appears to be possible, if desired, to eliminate the last traces of ammonia from the melt by catalytic decomposition at temperatures of the order of 550-600°C.

5. Removal of Ash

Coal extract feed will contain anywhere from 0.1 to 0.4 wt. % ash depending on its method of preparation. Ash must be periodically removed from the melt during its regeneration to prevent its build up. Several methods are available such as filtration after dilution with water and removal of zinc sulfide. It also may be removed by distillation of zinc chloride vapor from a side stream to leave an ash residue.

6. Overall Regeneration Scheme

The integration of the various process steps discussed above into a single regeneration scheme is illustrated in Figure 6. Appropriate operating ranges for each process step are likewise given.

A material balance around the operation is given in Table IV. The spent melt entering regeneration is assumed to be the same composition as that from the 5 stage coal extract hydrocracking run reported in a previous paper^(8b) {cf. Table IV}. The regenerated melt composition is adjusted such that the composition of the spent melt after hydro is consistent with elimination of 98.0% of the sulfur and 87.5% of the nitrogen from the feed extract, i.e., in accord with experimentally observed results in the 5 stage run.

The performance of the NH_3 decomposition tower was calculated from the data of Figure 5 assuming isothermal operation at 530°C , 4 theoretical stages and a total pressure of 1.5 atms.

In practice, one would have a temperature increase in the NH_3 decomposition tower since heat would be supplied by condensing zinc chloride vapor from the boiler. Thus, fewer stages would be required.

Recovery of NH_3 from the gases leaving the ammonia decomposer can be effected according to the data of Kurilov (cf. Figure 5) by scrubbing with a ZnCl_2 melt relatively concentrated in NH_3 at lower temperatures as shown in Figure 6.

The melt is readily decomposed to yield pure NH_3 gas at temperatures of the order of 400°C . Of course, other more conventional methods of ammonia recovery could also be used.

The above scheme is likewise adaptable to spent melts used in hydrocracking of coal itself. In this case the melt will contain a larger percentage of ash and accordingly more ash will have to be rejected in the vaporization step. In practice, a higher proportion of the melt will have to be vaporized, and this would be one of the disadvantages of using coal as compared with extract.

ACKNOWLEDGMENT

The sponsorship of the U. S. Office of Coal Research for this investigation is gratefully acknowledged.

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Presented Before the Division of Fuel Chemistry, ACS
Atlantic City, N. J., September 12-17, 1965.

TABLE I

Phase Separation of Organic Residue from Zinc Chloride Melt

Hydro Condition: $ZnCl_2$ /Extract, Wt. Ratio = 1
 Total Hot Pressure = 3000 psig
 Temperature = 750°F

Sample No.	1	2	3	4	5	6	7	8
Cum. Wt. % of Total Liquid Withdrawn	7.8	17.6	25.4	35.3	45.7	58.0	64.7	100
Cum. Wt. % of Total Gas Withdrawn	1.9	3.2	4.2	5.6	7.0	8.1	10.2	100
Type of Sample	Melt							

Lt. Oil
+ Gas

Analysis, Wt. % of Sample

Hydrocarbon Distillate	-400°C	5.5	10.5	7.8	16.2	9.4	9.8	21.9	100
Organic Residue	+400°C	18.0	20.3	21.6	15.4	18.2	17.3	29.5	--
$ZnCl_2$		62.7	54.4	58.2	56.9	61.8	61.9	40.4	--
$ZnCl_2 \cdot NH_3 + ZnCl_2 \cdot NH_4Cl$		9.3	10.8	8.5	6.5	6.8	6.8	4.0	--
ZnS		4.5	4.0	3.9	11.5	4.1	4.2	4.2	--

TABLE II

A. Phase Separation Studies with Water Addition

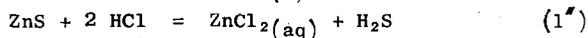
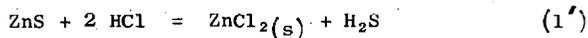
Wt. Ratio H ₂ O/Feed Temperature, °C	60 Minute Phase Separation Time Used											
	0.3		0.5		1.0		0.5		1.0		1.0	
	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase
Feed Melt	81.9											
ZnCl ₂	57.6	20.3	71.1	9.1	75.0	3.6	75.8	5.2	79.0	2.3		
ZnS	0.0	4.4	0.0	4.0	0.0	5.5	0.0	3.8	0.0	4.3		
NH ₃	1.0	0.3	1.0	0.2	1.0	0.0	1.3	0.1	1.1	0.0		
Extract	0.4	16.0	0.5	9.2	0.6	13.2	0.9	9.2	0.7	10.3		
Total	59.0	41.0	72.6	22.5	76.6	22.3	78.0	18.3	80.8	16.9		

B. Phase Separation with Water and Dimethylnaphthalene (DMN) Solvent Addition

Wt. Ratio H ₂ O/Feed Temperature, °C	0.56		0.22		250		Feed Melt Composition, Wt. %	
	0.56		0.22		250		Feed Melt Composition, Wt. %	
	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase	ZnCl ₂	NH ₄ Cl
ZnCl ₂	44.4	--	44.4	--	44.4	--	44.4	2.8
NH ₄ Cl	2.8	--	2.8	--	2.8	--	2.8	2.8
ZnS	2.3	0.5	2.3	0.5	2.3	0.5	2.8	50.0
Extract	1.4	48.6	1.4	48.6	1.4	48.6	Extract	
Total	50.9	50.1	50.9	50.1	50.9	50.1		

TABLE III

Equilibrium Data Compared for Reactions



Temperature, °C	50	66
<u>Normality of Equil. Mixture</u>		
HCl	2.6	0.68
ZnCl ₂	0.4	0.32
P _{H₂S} (atm)	1.52	0.10
P _{HCl} (atm) ⁽¹⁾	7.9 × 10 ⁻⁵	1.3 × 10 ⁻⁵
P _{H₂S} /P _{HCl} ² obs. for reaction (1'')	2.4 × 10 ⁸	5.9 × 10 ⁸
P _{H₂S} /P _{HCl} ² Calc. for reaction (1')	4.9 × 10 ³	1.5 × 10 ³

(1) From literature data at the measured acid concentration of International Critical Tables Vol. III, pg 301.

TABLE IV

Material Balance in Regeneration of Zinc Chloride Melt from
5 Stage Extract Hydro Run at 750°F - 3000 psig

Process Step	From Extract Hydro	From ZnS Decomposer	MgCl ₂ from Decanter	From NH ₄ Cl Decomposer	From Condenser	From Primary NH ₃ Decomposer
Temperature, °C	393	~ 100	200	427	400	530
No. of Stages	5	1	1	NC	1	4
<u>Moles/100 lbs Extract Fed to Hydro</u>						
<u>Liquid Phase</u>						
ZnCl ₂ (1)	0.197	0.252	0.252	0.252	0.0024	0.343
ZnCl ₂ ·NH ₃ (1)	0.018	0.018	0.018	0.129	0.0078	0.038
ZnCl ₂ ·NH ₄ Cl(1)	0.111	0.111	0.111	--	--	--
ZnS(s)	0.055	--	--	--	--	--
+400°C Organic Residue (lbs)	17.4	17.4	--	--	--	--
<u>Gas Phase</u>						
Stripping Gas	--	--	--	NC	0.550	0.550
NH ₃	--	--	--	--	0.091	0.0988
ZnCl ₂ (v)	--	--	--	--	--	0.0102
H ₂ S	--	0.055	--	--	--	--
HCl	--	--	--	0.111	--	--

(1) Percent of sulfur released from extract feed as ZnS = 98.0

(2) Percent of nitrogen released from extract feed as NH₃ + NH₄Cl = 87.5

Figure 1
APPARATUS FOR EQUILIBRIUM STUDIES

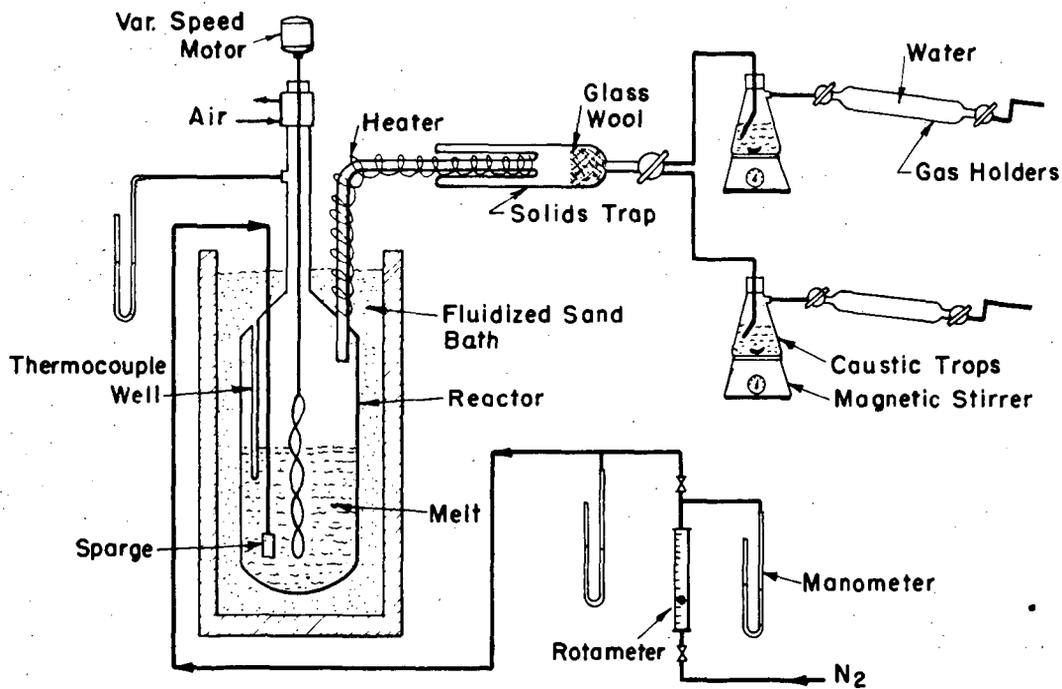


Figure 2

EQUILIBRIUM PARTIAL PRESSURE OF HCl
VS
% NH₄Cl DECOMPOSED

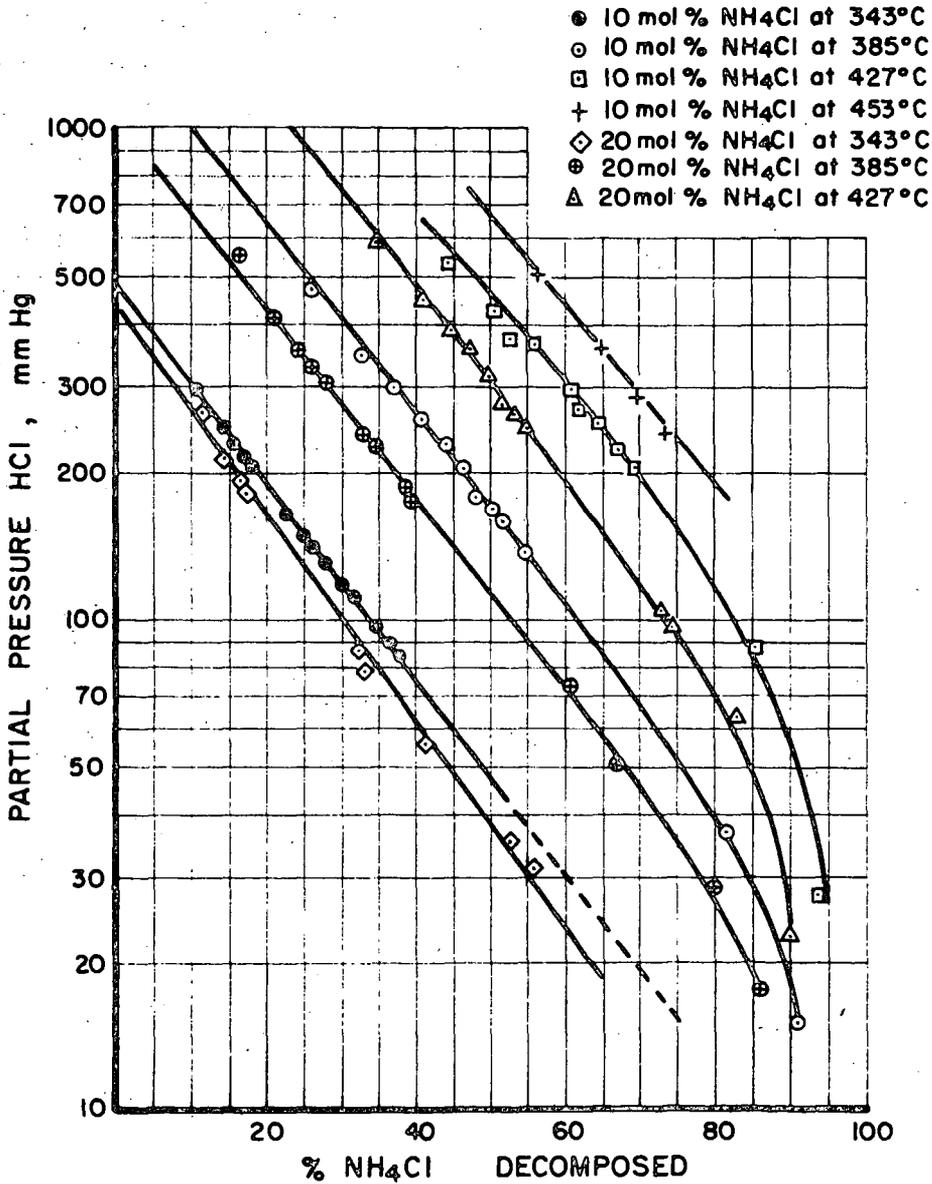


Figure 3
EQUILIBRIUM CONSTANT FOR REACTION
 $ZnCl_2 \cdot NH_4Cl = ZnCl_2 \cdot NH_3 + HCl$

Initial Concn. NH ₄ Cl Mol%	Temp. °C
○ 10	427
◊ 10	385
◻ 20	427
◻ 20	385

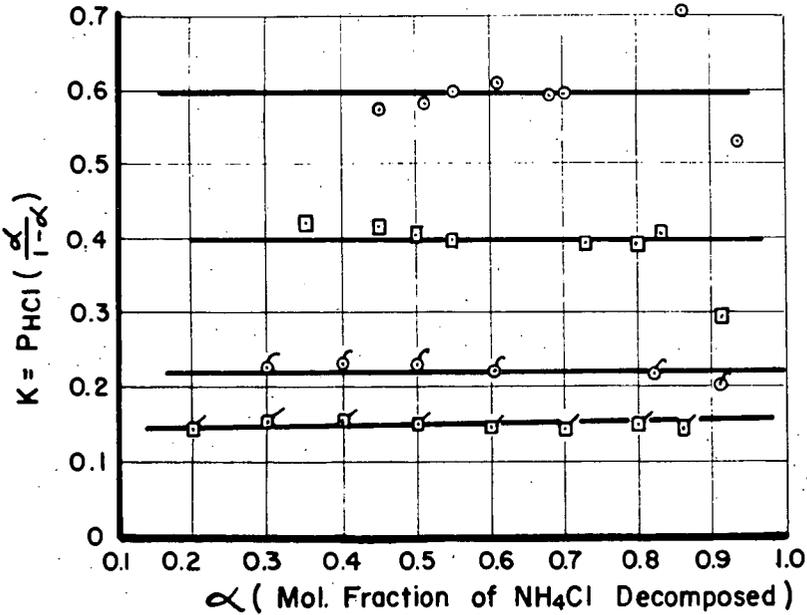


Figure 4

EFFECT OF TEMPERATURE ON
HCl EQUILIBRIUM PARTIAL PRESSURE

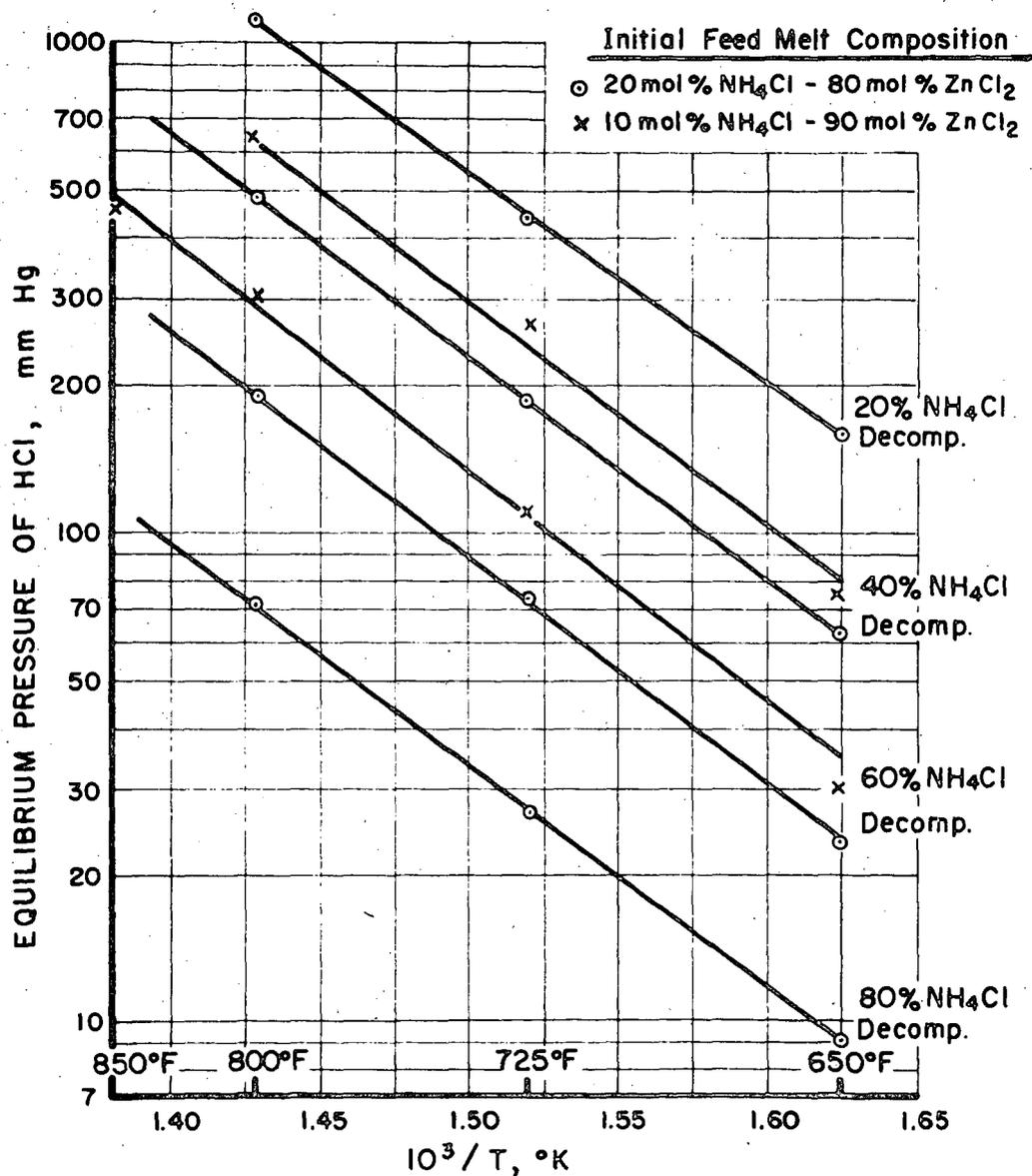


Figure 5

**SUMMARIZED DATA ON DISSOCIATION
PRESSURE OF NH₃ OVER ZnCl₂ MELTS**

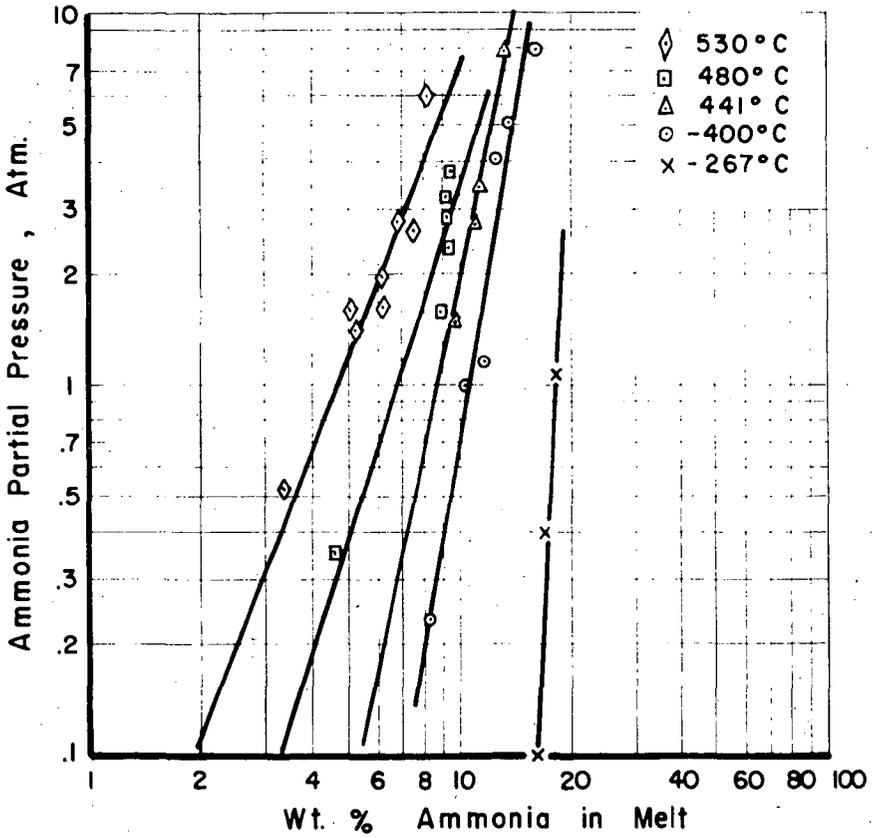
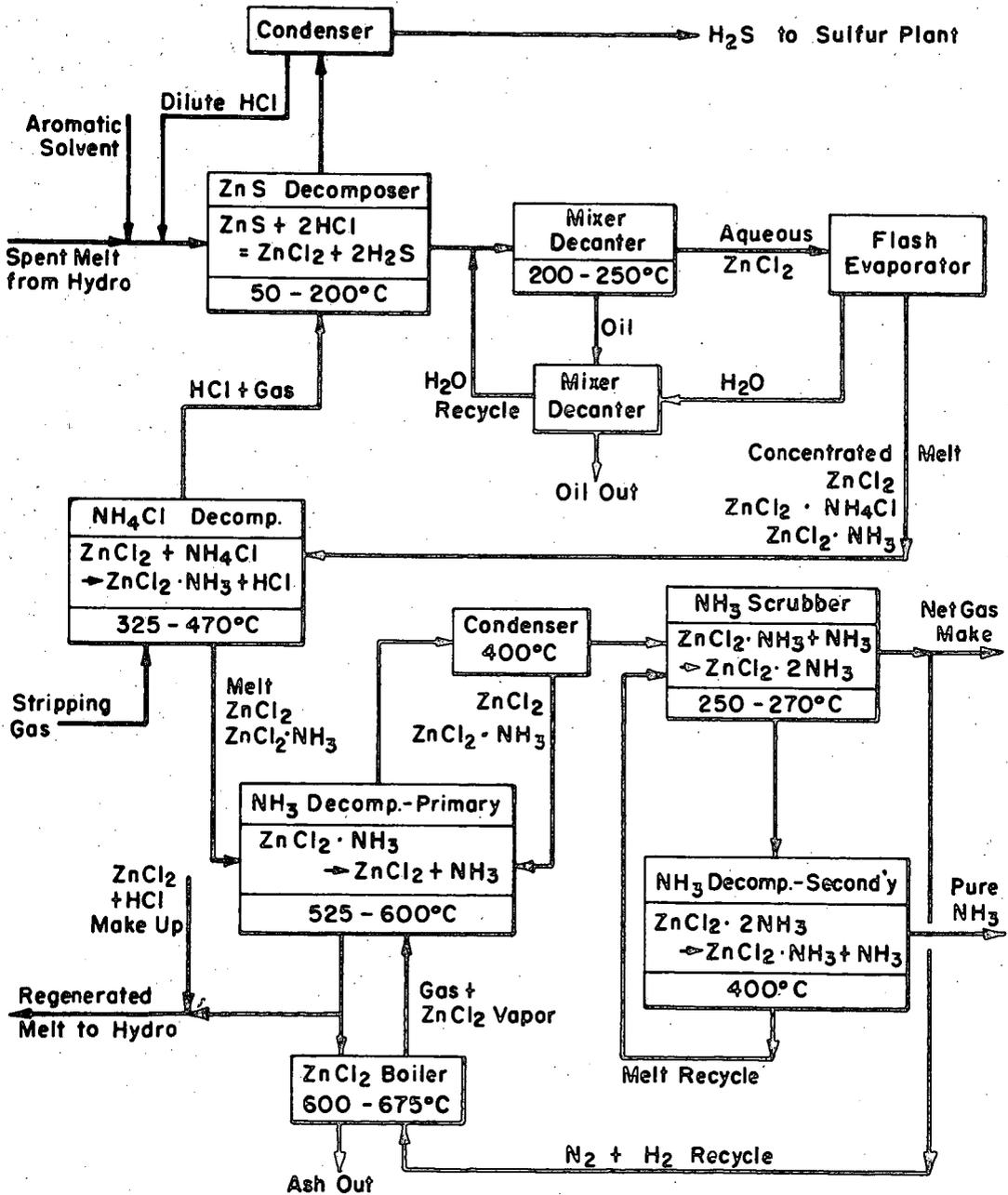


Figure 6

SCHEMATIC DIAGRAM OF REGENERATION SCHEME



Elevated Pressure Adsorption of Methane on Activated Carbon;
Effects of Contaminant Gases and Repeated Cycling

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INTRODUCTION

Bureau of Mines interest in methane adsorption was developed from research on hydrogasification of coal to produce synthetic pipeline gas. The product from hydrogasification consists principally of methane and hydrogen^{2, 6}, the methane content varying from 5 to 80 percent depending on process variables. The minor constituents are nitrogen, carbon oxides, sulfur compounds, unsaturates, higher molecular weight hydrocarbons including aromatics, and water vapor. Synthetic pipeline gas with a heating value of approximately 1,000 Btu's can be produced from hydrogasification product by recovering the methane. The Bureau of Mines has reported that estimated capital and operating costs for separating methane from mixtures of methane and hydrogen are lowest if the methane is adsorbed by activated carbon⁸. The estimate, however, was based on extrapolated data⁵ for the adsorption of pure methane at relatively low pressures. The objective of this investigation was to establish adsorption isotherms for methane on activated carbon at 40° C and pressures of 14.2 to 800 psia and study the tendency of activated carbon to lose its adsorptive capacity for methane when the methane is contaminated with other gases and/or there is repeated cycling.

Effects of adding benzene, hydrogen, ethylene, or hydrogen sulfide were investigated. These gases were chosen as contaminants because they are in the gaseous mixture produced by hydrogasification. Two of the contaminant gases, benzene and hydrogen, used in the experiments were given concentrations similar to those found in a hydrogasification product. The other two contaminants, ethylene and hydrogen sulfide, were given much higher concentrations than would be found in a hydrogasification product in order to simulate rapid poisoning of the adsorbent.

The adsorptive capacity of activated carbon can be affected by side reactions. Activated carbon may act catalytically to convert hydrogen sulfide to free sulfur in the presence of trace amounts of oxygen, and the free sulfur may occupy space that could be taken up by the methane.¹

APPARATUS AND PROCEDURE

Some of the main components of the fixed-bed adsorption unit are shown in figure 1. The adsorber was made of type 304 stainless steel as were the valves, fittings, tubing, and gas collection reservoirs, because of their contact with hydrogen sulfide. The adsorber was 24 inches long with 1/2-inch outside diameter and 3/8-inch inside diameter. It had a maximum working pressure of 1,500 psi and a maximum working temperature of 450° C. During desorption, heat was supplied electrically using the adsorber wall as an electrical resistor. Power for heating was supplied by a 7.5 KVA, 10:1 step-down transformer. During the cooling cycle, the adsorber was rapidly cooled along its entire length by air blown from a series of small nozzles.

During the rapid cycling studies, the adsorption, desorption, and cooling cycles were automatically controlled by a time cycle controller. A complete cycle consisted of a 9-minute adsorption period at 40° C, 6 minutes desorption at 450° C, and 3 minutes cooling.

Figure 2 is a schematic flow diagram of the rapid cycling, fixed-bed adsorption system. The desired feed gas of known composition is supplied to the unit from high-pressure storage cylinders. The gas flow rate is measured by pressure drop through a calibrated capillary manometer. The gas saturator was used to add benzene to the feed gas when the contaminating effect of benzene was studied.

A weighed sample of fresh activated carbon was placed in the adsorber prior to each series of experiments. The activated carbon was degassed under vacuum for 2 to 3 hours at 450° C. At the end of this period the pressure in the adsorption chamber, measured by a McLeod gage, was about 15 microns Hg. The "dead space" in the reactor system was the volume of the adsorption chamber bounded by three solenoid valves, SV-1, SV-2, and SV-3. It represented the adsorbent pore volume, the interparticle void space, plus the volume of the apparatus capillary lines inside the respective boundaries. Dead space was determined by introducing measured amounts of helium at atmospheric pressure into the evacuated adsorption chamber, noting the equilibrium pressure, and applying the ideal gas law. Adsorption of helium was assumed to be negligible under these conditions.

In determining the amount of methane adsorbed for the pure methane experiments (static studies), methane was fed into the adsorption chamber until equilibrium conditions were attained. Equilibrium was attained rapidly, in some cases within 15 minutes. The gas was then desorbed from the adsorption chamber into a 500-cc calibrated collection reservoir. The desorption temperature was 450° C for all the experiments. A slow helium purge was also used in conjunction with the high temperature to remove the last traces of methane. The amount of methane adsorbed on the activated carbon was the difference between the total methane collected and that contained in the dead space.

In the mixture experiments (dynamic studies), it was assumed that methane equilibrium was attained in approximately the same length of time required during the pure methane experiments (static studies). After methane equilibrium was attained, the gas remaining in the dead space and on activated carbon's surface was desorbed into the 500-cc calibrated collection reservoir. The amount of methane adsorbed was determined in a manner similar to that used for the static studies.

The ideal gas law was used for computing the amount of adsorbed gas when the total adsorption pressure did not exceed 50 psi. Generalized compressibility factors^{9/} were used in conjunction with Amagat's law when total pressure exceeded 50 psi.

All gases were analyzed by chromatography and mass spectrometry. The methane used in the experiments contained 0.2 percent ethane and 0.1 percent nitrogen. The adsorbent was a 12x30 mesh Pittsburgh Coke and Chemical Co. Type BPL activated carbon manufactured from various grades of bituminous coal combined with suitable binders.

RESULTS AND DISCUSSION

When adsorption takes place in a unimolecular layer, or part of a layer, the data can often be fitted satisfactorily by means of the simple Langmuir equation^{7/}

$$x/m = \frac{a b P}{1 + a P}$$

In this formula

- x = weight of gas adsorbed.
- m = weight of solid adsorbent.
- P = Partial pressure of the gas in question at equilibrium.
- a, b = experimental constants.

The Langmuir equation is based on the assumption that the molecules of the adsorbed gas are present on the surface of the adsorbent as a monolayer. The greater the fraction of the surface covered by the monolayer, the less tendency there is to accumulate more molecules and the greater the partial pressure must be to continue such accumulation.

The Langmuir formula may be rewritten as the equation of a straight line,

$$P/(x/m) = (1/b) P + 1/(a b).$$

The experimental constants a and b can be calculated if the plot of $P/(x/m)$ versus P is a straight line. Figure 3 shows Langmuir plots of our experimental data and data of four other investigators, Per K. Frolich^{4/},

L. Szepesy^{11/}, G. C. Ray^{10/}, and R. J. Grant^{5/}. Curve 5 represents Grant's extrapolated data. These extrapolated data were used in our original cost estimates.

Plots of both Szepesy's and our data, curves 2 and 3, produced straight lines. The upper portion of Frolich's data, curve 1, is also a straight line. The experimental constants for curves 2 and 3 become:

1) Curve 2: $a = 9.64 \times 10^{-3} \text{ psia}^{-1}$, $b = 7.41 \text{ g/100 g}$.

2) Curve 3: $a = 12.85 \times 10^{-3} \text{ psia}^{-1}$, $b = 5.56 \text{ g/100 g}$.

Freundlich's equation, $x/m = a P^{1/n}$, is used frequently to correlate adsorption data. The letters x, m, and P have the same meaning as in the Langmuir equation, and the letters a and 1/n represent empirical constants.

The validity of the formula for the experimental data can be tested by plotting the logarithm of x/m against the logarithm of P, since rewriting the formula in its logarithm form, $\log(x/m) = \log a + (1/n) \log P$, gives the equation of a straight line.

Figure 4 shows Freundlich plots of our experimental data and data of the four other investigators previously mentioned. None of the curves obeys the Freundlich equation.

Table 1 shows the effect of 76.5 percent hydrogen in the methane feed gas upon activated carbon's adsorptive capacity for methane. In these series of experiments, two methane partial pressure levels were investigated, 50 and 300 psia. Activated carbon's equilibrium capacity for methane was reduced 10.0 and 22.8 percent, respectively, owing to the presence of hydrogen. Experiments with a methane-hydrogen mixture showed that the selectivity of the carbon for methane over hydrogen was 11:1 at 50 psia partial pressure, and 28:1 at 300 psia.

Figure 5 shows the effect of methane contamination and repeated cycling upon activated carbon's adsorptive capacity of methane. Benzene, hydrogen, ethylene, and hydrogen sulfide were the contaminants tested. After the first adsorption step, all the contaminants reduced the capacity of activated carbon for methane. The initial reductions in capacity for methane owing to the presence of the contaminants are given in percent in table 2. The presence of 8.3 percent hydrogen sulfide produced the greatest initial loss of capacity, reducing the carbon's capacity for methane by 53 percent. Benzene, hydrogen, and ethylene reduced the methane capacity of the carbon by 13, 25, and 37 percent, respectively.

Additional adsorption-desorption cycles using the contaminated methane feed gases incurred no further decrease in carbon capacity for methane except in the tests using 10.3 percent ethylene in the methane feed gas. After 150 cycles, activated carbon's capacity for methane was reduced an additional 13 percent from 37 to 50 percent.

TABLE 1.- Effect of hydrogen upon activated carbon's adsorptive capacity for methane

Feed gas	Adsorption temperature, °C	equilibrium pressure, psia	Activated carbon's capacity for methane,	Activated carbon's capacity for hydrogen,	Selectivity, Carbon capacity(CH ₄) Carbon capacity(H ₂)
			<u>g CH₄</u> <u>100 g carbon</u>	<u>g H₂</u> <u>100 g carbon</u>	
a) CH ₄ ^{1/}	40	50	2.49	--	--
23.7 pct CH ₄ b) + 76.3 pct H ₂	40	50	2.24	0.02	11:1
a) CH ₄ ^{1/}	40	300	5.49	--	--
23.7 pct CH ₄ b) + 76.3 pct H ₂	40	300	4.23	0.15	28:1

^{1/} Containing 0.2 pct C₂H₆ and 0.1 pct N₂.

TABLE 2.- Reduction in activated carbon's capacity for methane by contaminating gases and repeated cycling ^{1/}

Contaminating gas, vol-pct	Percent		Saturation of activated carbon with impurity
	Initial reduction in capacity for methane (without recycling)	Reduction in capacity for methane after 150 cycles	
0.35 C ₆ H ₆	13.0	14.0	10.0
76.3 H ₂	25.0	25.0	100.0
10.3 C ₂ H ₄	37.0	50.0	75.0
8.3 H ₂ S	53.0	53.0	100.0

^{1/} Conditions: Adsorption temperature 40° C; Methane equilibrium pressure 300 psia.

In these contaminating and cycling tests, hydrogen and hydrogen sulfide were the only two contaminants that completely saturated the activated carbon. Benzene and ethylene only reached 10 and 75 percent carbon saturation, respectively. In all of the tests conducted, methane attained equilibrium conditions or 100 percent saturation before desorption was initiated. Degree of saturation was determined through adsorber tail gas analyses.

Experiments were conducted about five times for each pure methane equilibrium point. Standard deviation from the mean value was $\pm 1-2$ percent for these experiments. Standard deviation for the methane-hydrogen mixture experiments conducted at the two partial pressure levels was ± 15 percent. Greater scattering of data occurred when the small quantities of hydrogen adsorbed were being determined.

CONCLUSIONS

1. Increased total pressure favors the preferential adsorption of methane from methane-hydrogen mixtures. However, methane is less strongly adsorbed from the mixture than when it is present at the same partial pressure in the pure state. Lower values for methane adsorption at high partial pressures were found experimentally than those extrapolated from existing data at lower pressures.

2. Each impurity of hydrogasification product gas tested decreased activated carbon's capacity for methane. Although the carbon was not completely saturated with benzene and ethylene, these impurities still contributed significantly to the initial lowering of the adsorbent's capacity for methane.

3. Repeated cycling, up to 150 cycles, in the presence of the contaminants did not further decrease activated carbon's capacity for methane except when ethylene was added.

4. These results indicate that the cost estimates reported earlier^{8/} were too low because the extrapolated values for methane adsorption were too high. The efficiency of activated carbon in adsorbing methane is lowered by other gases mixed with the methane and, when ethylene is present, by repeated cycling. However, for most of the cases of separation investigated (CH_4 concentrations of 5, 20 and 50 pct), the economics of adsorption by activated carbon are now considered to be approximately the same as separation by liquefaction of methane.

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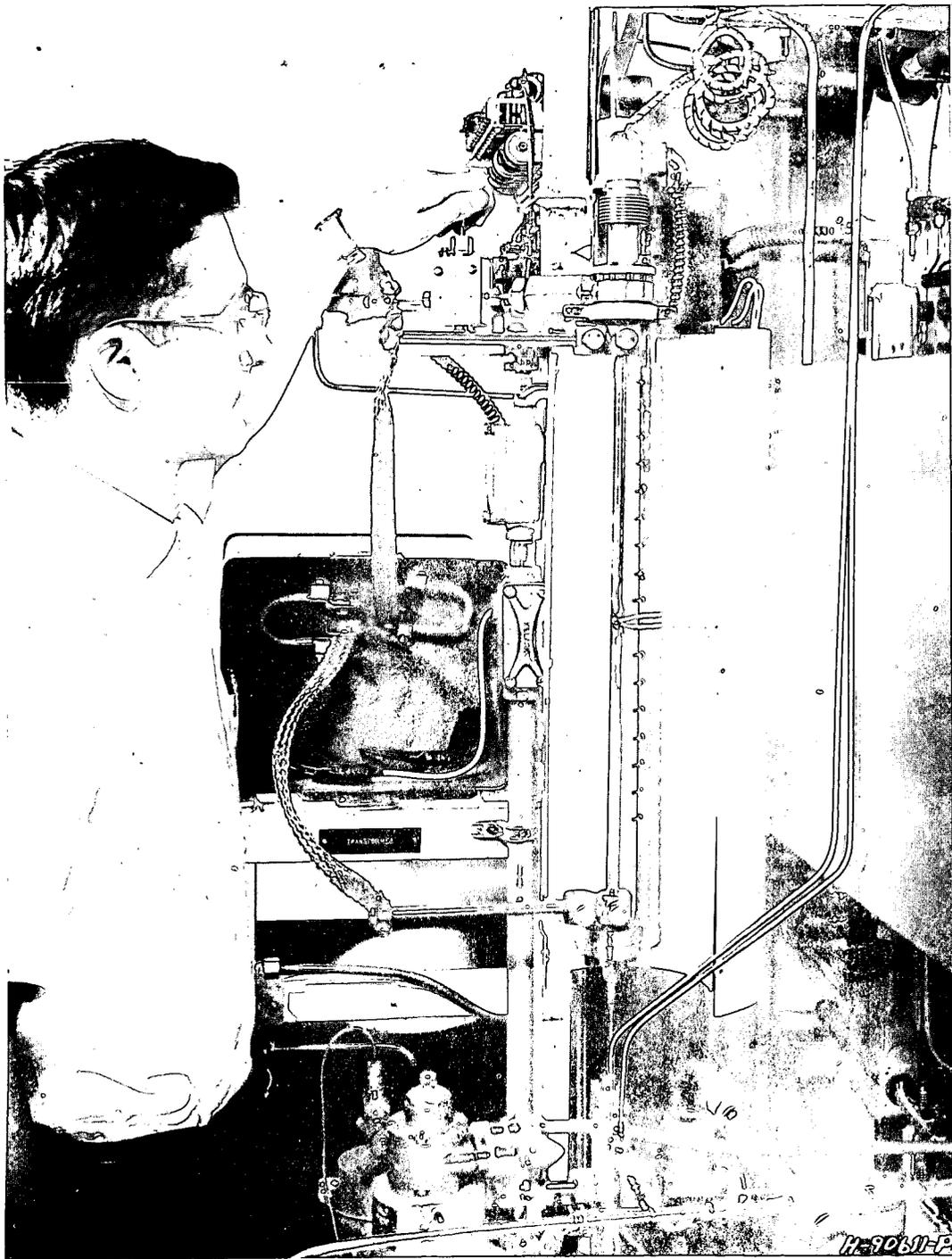


Figure 1.-RAPID CYCLING, FIXED BED ABSORBER

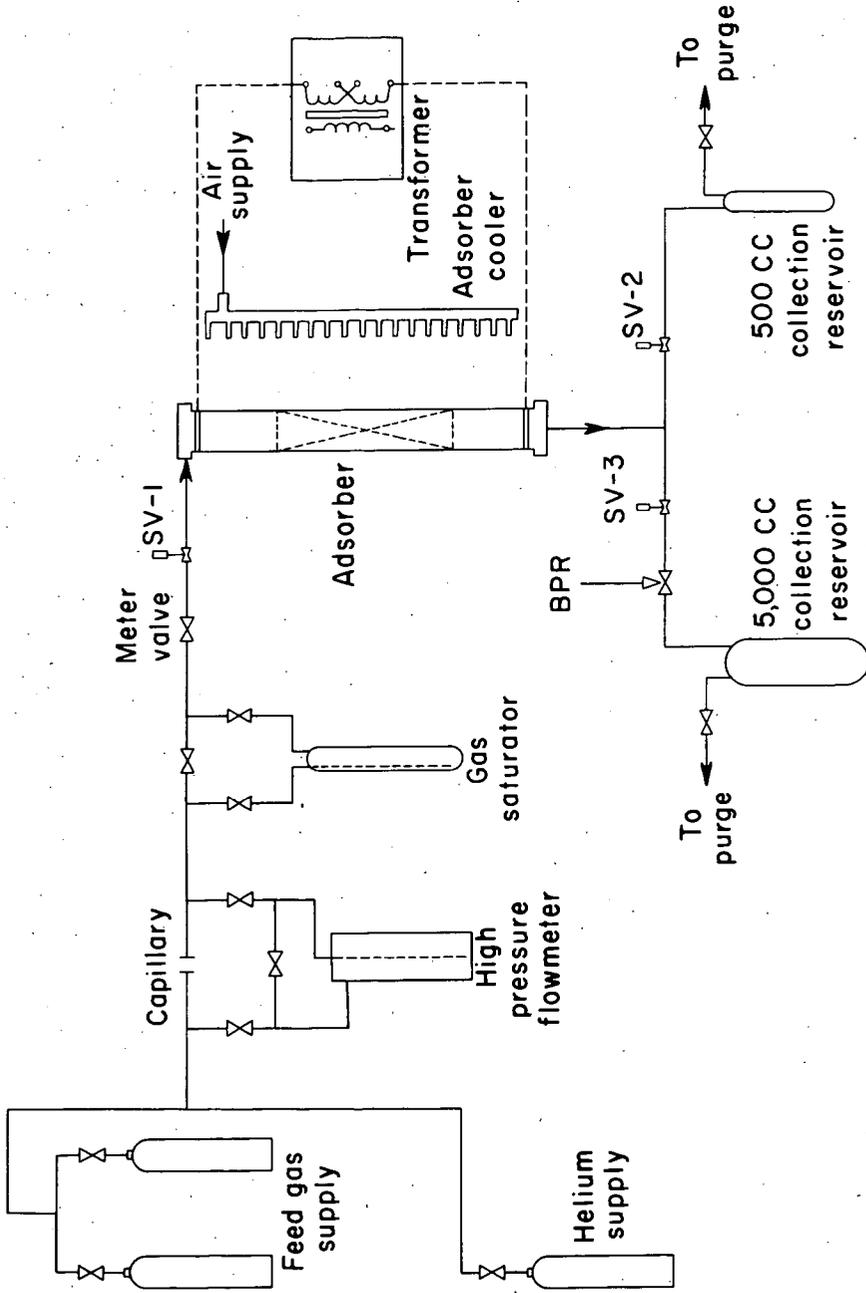


Figure 2.-Overall flowsheet of bench-scale adsorption unit.

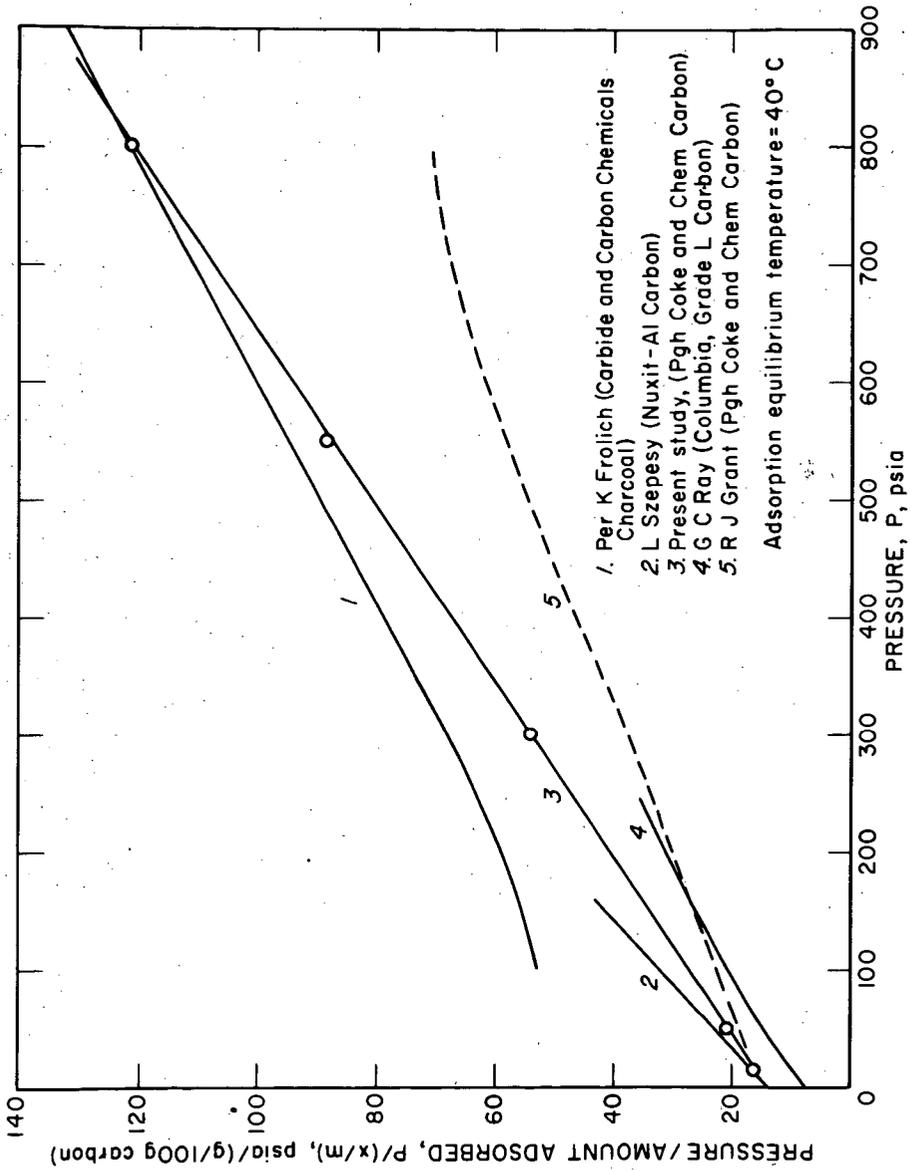


Figure 3.- Adsorption isotherms for methane on various types of activated carbon, Langmuir plots.

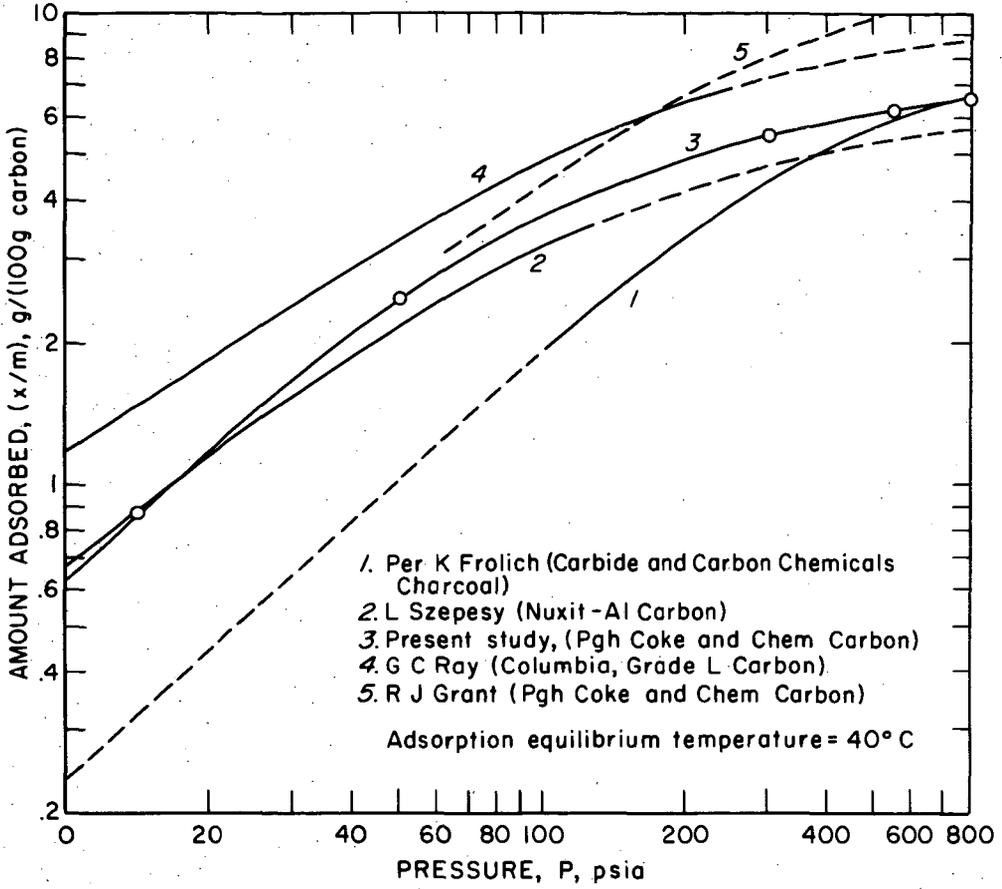


Figure 4.-Adsorption isotherms for methane on various types of activated carbon, Freundlich plots.

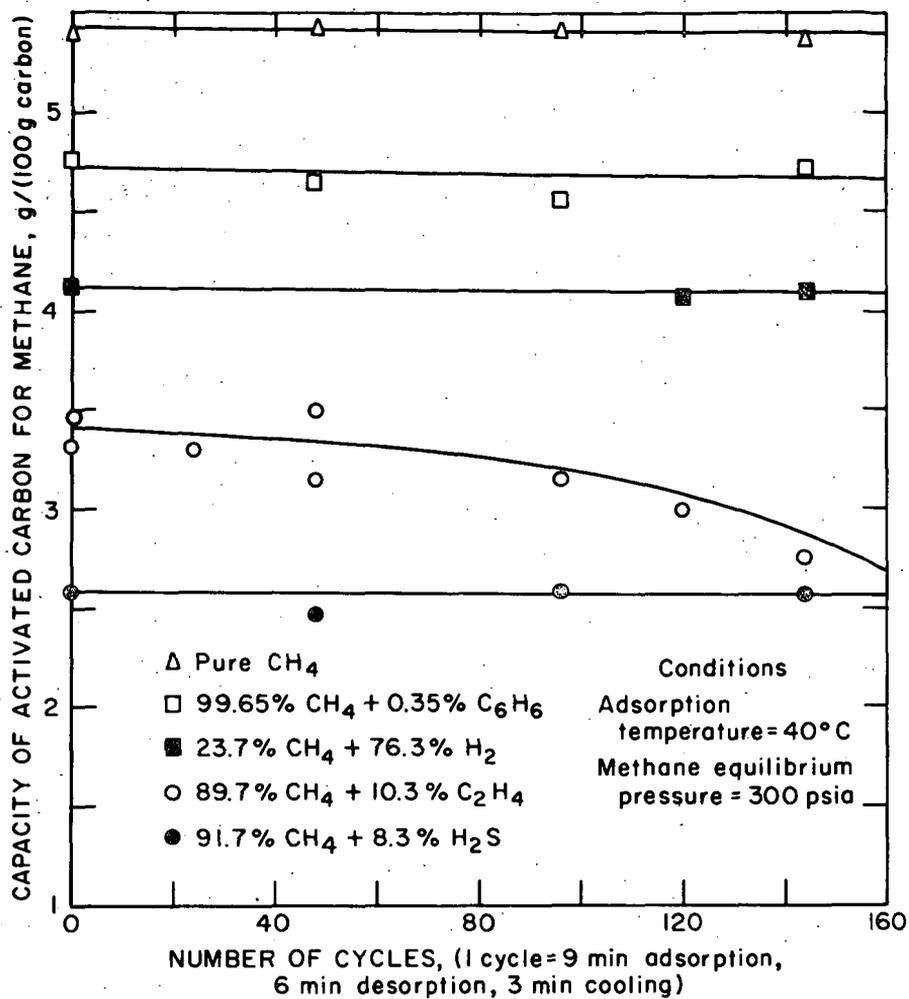


Figure 5.—Effect of contaminating gases and repeated cycling upon activated carbon's capacity for methane.

HOT APPLIED COAL TAR COATINGS

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INTRODUCTION

The very high aromaticity of high temperature coal-tar pitch accounts for many of its unusual physical and chemical properties which make it the preferred raw material for a wide variety of applications. High temperature coal-tar pitch is practically inert to the action of water and neither absorbs or transmits it. High-temperature coal-tar pitch is highly resistant to attack by bacteria and fungi. This property, together with its moisture resistance, make it eminently suitable for roofing; waterproofing; coating of buried steel pipe lines to protect them from corrosion action of wet soil; lining of water pipes, tanks, etc.

COAL-TAR PITCH BASE FOR ENAMELS

Normal coal-tar pitch is somewhat sensitive to changes in temperature. It is comparatively hard and brittle at low temperatures and it tends to soften and flow at high temperatures. It exhibits simple Newtonian flow and is subject to cold flow, i.e., it is deformed by the continued action of a small applied force and in direct proportion to the amount of force applied.

In the early 1930's, a means was found to reduce the susceptibility of coal-tar pitch to temperature change. A "plasticized" pitch was produced by digestion of bituminous coal in coal tar and high boiling coal-tar distillate oils. These plasticized pitches show much reduced susceptibility to temperature changes. They are comparatively soft and are not brittle at low temperatures, and at the same time, they do not soften too readily and flow at high temperatures. In rheological terms, they exhibit complex flow. They can be deformed by the action of strong forces but are to some degree rubbery and resilient and they are very little affected by the action of small forces of the order of 2 to 5 psi which are the estimated order of soil distortion forces at work on a buried, shielded pipe coating. (1)

Figure 1 and Figure 2 summarize pressure deformation tests made by Allied Chemical. These tests were made by immersion of an apparatus, in constant temperature water baths maintained at 77°F and 115°F, in which a weighted $\frac{1}{4}$ " diameter blunt monel metal rod rests on a flat dish filled with enamel. These tests show that despite the apparent softness of the plasticized enamel it is more resistant to the action of deforming forces in the low stress range. The tests at 77°F, which can be related to normal temperature conditions of soil forces on buried pipe, show less deformation for the plasticized enamel in the 2 to 5 psi range. The tests at 115°F can be related to deforming forces in handling coated pipe in hot weather or to soil forces on buried pipe in hot line service. The plasticized enamel shows far superior resistance to deformation when deforming forces are comparative light.

HISTORY

Coal-tar coatings have been used for over 100 years to protect ferrous metals against underground corrosion. In 1913, an early form of coal-tar enamel was used in protecting the gates, locks and penstocks of the Panama Canal. Examination after 35 years of service showed them to be in perfect condition. The first application of coal-tar enamel to steel pipe for potable water was made in New York in 1914. At the last count this line was still in operation after over 45 years of service. In the 1930's, AWWA type enamels were used extensively in water lines in many large scale projects particularly in the Far West. These installations are still giving trouble-free service and the coal-tar enamels are virtually unchanged after service of over 30 years. Many excellent general articles have been presented on coal tar enamels. (2,3,4,5,6,7)

MINERAL FILLERS

In the production of coal-tar enamels, usually around 25 to 30% of inert, fine mineral fillers are added to the pitch to improve mechanical strength such as resistance to impact and resistance to deformation from soil forces. Fillers also help to reduce flow at high temperature and tendency to crack at low temperatures.

SPECIFICATIONS

Typical specifications for various grades of coal tar enamels are shown in Table 1. These enamels differ chiefly in the variations in atmospheric or service temperature ranges they will withstand--either from cracking at low temperatures or flow at deformation at high temperatures.

Unplasticized Enamel: A narrow range enamel - exposure range is 30 to 120°F. This grade of enamel is hard and highly resistant to deformation from soil forces. It also has very high resistance to moisture and soil chemicals. It is easy to heat and apply, and is best suited for "over the ditch" application where it will not be subjected to extremes in atmospheric temperatures in storing or rough handling in shipping.

Partially Plasticized: A modified grade to better withstand variations in temperatures. Exposure range is 0 to 140°F. It is a good all-purpose enamel. It is easy to apply and is suitable for either shop coating or over the ditch application.

SPECIFICATIONS

Plasticized Enamels:
Regular Grade

A fully plasticized enamel with a wide exposure range of -20 to 160°F. It is resistant to shock and deformation and is less subject to damage in handling. With wide exposure range, it can be stored for long periods without damage to coating from extremes in temperatures.

AWWA Grade:

A fully plasticized enamel with a wide range of -20 to 160°F. It is softer than Regular Grade and is more flexible and better suited for large diameter pipe. It is specifically designed to meet exacting requirements of AWWA. It also finds application on gas and product lines where very low temperatures might be encountered in storage of coated pipe.

Hotline Grade:

A fully plasticized enamel but higher in softening point and harder so as to better withstand high temperature service. Exposure range is 0 to 180°F. It is designed and recommended for:

1. Gas pipelines, at the discharge side of pumping stations where gas enters the pipe at temperatures above 120°F.
2. Warm swampy areas, salt flats, desert beds and other places where excessive soil stress is present.
3. Areas where backfill and trenches are rough, full of stones and other objects which normally penetrate softer coatings.
4. Hot oil lines and lines encapsulating electric cables where temperatures are consistently high most of the time, but do not exceed 180°F or 200°F for short term exposure.

P R I M E R S

Primers for the enamels must be capable of application by spraying, rolling, or brushing. They must dry in a reasonable period of time and they must give a strong bond with the enamel.

Usually the primers consist of a pitch base, similar to that used in making the enamel, cut back with an aromatic solvent.

There are available quick-drying primers that in addition to developing a strong bond, have the added advantage of very quick-drying properties. These quick-drying primers are chemical as well as conventional coal-tar pitch based primers.

REINFORCEMENT AND OUTER WRAP

It is general coating practice to pull a glass mat into the hot enamel as a reinforcement and the outer side of the coating is protected with a tar saturated asbestos felt.

The glass mat is composed of light weight glass fibers randomly oriented. The sheet is very open and is easily pulled into the hot enamel. This mat acts as a reinforcement for the enamel coating and helps to resist cracking in handling.

The tar saturated asbestos felt outer wrap can be a standard weight of approximately 15 lbs. per 100 sq. ft. or a light weight at 9.0 lbs. per 100 sq. ft. The standard weight has a higher tensile strength than the light weight and is the preferred type. As an added strengthening agent glass fiber can be imbedded into the asbestos felt at spaced intervals (usually $\frac{1}{4}$ ") across the sheet. The asbestos felt outer wrap is intended to minimize damage when handling the coal-tar coated pipe as well as to protect it from damage during the back filling operation and from soil forces in service.

A Kraft Wrapper is usually applied as a finishing protective cover.

A P P L I C A T I O N

Coal tar enamel coatings are both mill and field applied. Specifications for enamel coatings systems from simple single enamel coat to multiple enamel coats with glass reinforcement and asbestos shields are shown in Table 2. The severity of service conditions determines the system to be used.

M I L L A P P L I C A T I O N

This application may include interior lining in addition to the exterior coating and wrapping.

The pipe is sand or grit blasted to remove excess rust and mill scale and a coating of primer is applied.

Usually in applying the enamel the pipe moves thru the coating equipment with a rotating motion and the hot enamel is flowed onto the pipe. It is also general practice to pull a glass wrap into the coating as well as to apply an outer protective wrap when applying the hot enamel.

Interior linings for water lines are centrifugally applied by flowing hot enamel into the pipe while it is rotating at a speed of about 900 lineal ft. per minute.

FIELD APPLICATION

In Field Application, the coating is applied with specialized equipment that rides on the pipe. The pipe is brought to the right of way and "strung" in place; the welders then weld the pipe sections together; the cleaning unit consisting of rotating wire brushes removes mill scale and rust just prior to application of the primer. Following the primer unit is a similar unit where the hot melted coating is applied to the pipe with a glass wrap and a protective outer wrap is applied with the same equipment. The protected pipe is then installed by lowering into the ditch.

MOISTURE ABSORPTION

Minimum moisture absorption is the most important single property that a good coating must have. Minimum moisture absorption goes along with high electrical resistivity. If a coating does not absorb water, it does not become electrically conductive; and therefore, cost of current to protect the pipe cathodically is reasonably low. Minimum moisture absorption is necessary in order to have a continuous strong bond. If a coating absorbs water, and this water gets to the interface between enamel and primer, the bond is destroyed. Minimum moisture absorption is also tied with resistance to soil chemicals. These soil chemicals are water-borne and will never do any damage unless they penetrate the coating, and this will only be the type of coating which

will absorb water.

Water absorption of coal-tar enamels is extremely low. NACE Committee T-6A on Thermoplastic Coal Tar Base Linings reports that after 6 years immersion, coal-tar enamels, at approximately 100 mils thickness, show an absorption of only 1.7 to 2.3 gms. per square foot or 0.5 to 0.6% by weight.

Water absorption tests at Allied Chemical for a 2-year immersion period show 1.4 gms. per sq. ft. for unplasticized enamel and 3.0 gms. for plasticized enamel. Test results are shown in Figure 3. It will be noted that the absorption curve is levelling out as the time of the test progresses. These tests were made using 316 stainless steel plates which were coated by dipping in hot enamel.

High moisture absorption in time results in the coating becoming electrically conductive, giving rise to high current consumption and high cost for cathodic protection. This high moisture absorption in time results in complete chemical degradation. The high moisture absorption also results in complete loss of bond to the pipe.

Dr. J. O. Harris of Kansas State University determined actual water content by the Dean Stark Method on samples of coal-tar and asphalt enamels removed from active buried pipe lines after up to 29 years service. (9) Analyses of a chart presented in Dr. Harris' paper shows that for 28 coal-tar enamels in the test, service varied from 3 to 29 years with an average of 14.1 years service. The maximum moisture content of all coal-tar enamels was 0.3%. The 19 asphalt enamels in the test varied from 7 to 26 years in service with an average of 13.7 years. The moisture content of the asphalt enamels varied from 3 to 19% with an average of 12.4%.

Dr. Harris' work clearly shows the necessity for long-term water absorption tests for reliable evaluation of pipe coatings.

ELECTRICAL RESISTANCE

High electrical resistance is necessary in the coating so that there will be a minimum amount of current required for cathodic protection. Furthermore, this high electrical resistance must be not only high initially, but must remain high through years of service. Most corrosion engineers and pipeline operators feel that a good coating tested when it is first installed in the ground should test from $\frac{1}{2}$ to 2 megohms per square foot. A generous allowance is made here for some loss of resistivity due to damage in handling prior to laying the pipe, moisture absorption in storage prior to burial, and to damage from burial operations and backfilling. In an excellent article, the IEEE Guide for Selecting Coatings for Pipes of Pipe-Type Cable Systems (10) a comparison is made of bituminous coatings for pipe cable systems. Reinforced Coal-Tar Enamel, Hot-Line Grade, is rated at 1 megohm per square foot when installed and still 1 megohm after 5 years in wet soil. Reinforced asphalt enamel is rated at 1 megohm when installed and 0.1 megohm after 5 years in wet soil. Asphalt mastic is rated at 10 megohm when installed but 0.1 megohm after 5 years in wet soil. In terms of current requirements

for cathodic protection--this would mean that for a mile of 8" pipe, 3 milliamps would be required initially and after 5 years of service, coal tar coated pipe would still require only the same current. The asphalt coatings would require 30 milliamps after 5 years service. (10, 11, 12).

In our own laboratory work, specimens of coated steel are very carefully prepared and are of the proper and specified film thickness. There are no thin spots where felts or glass cut into the coating, no damage from handling or installation in the ground, and true resistivity of the coating itself are determined. In this type of test, initial resistivities are consequently far higher than are obtained in a commercial pipe installation.

Two series of tests were run in Allied's laboratories. In the first series a number of enamels were tested at approximately $3/32$ of an inch thickness of coating. The enamels were immersed for one year in N/10 Sodium Chloride solution. Initially all enamels tested well over 1,000 megohms per square foot. Results on coal-tar enamel show very high electrical resistance after the one year immersion period. Test results are shown in Table 3.

In another series of tests in which coal-tar enamels of $2/32$ of an inch thickness were subjected to 10 years of continuous immersion in a 5% sodium chloride solution, resistivity was more than 50 megohms per square foot.

Since the resistivity of coal-tar enamels is extremely high, and remains at this high value if the coating is not distorted or damaged, it is the imperfections in the coating and the resistivity of the soil water contained in these imperfections that control the magnitude of the coating resistance that will be measured in the field.

CONTINUOUS STRONG BOND

This is a corollary of the chemical inertness of coal tar pitch. Coal tar pitch shows extremely low moisture absorption, is highly resistant to bacterial deterioration, and highly resistant to soil chemicals. As a result, the coating remains practically unchanged through years of service. No moisture can get through the coating to the pipe and the bond remains firm and strong throughout long years of burial. Coal tar coated pipelines have been dug up after being in service for 20-30 years and more and we find the coating unchanged and the bond strong. The coal tar coating must be laboriously removed and chipped off with a hammer and scrappers.

A Southern Natural Gas line recently dug up and cleaned at the Harvey, Louisiana, yard of the Shamrock Pipe Coating Company is a typical example of coal tar coating which was practically unchanged after 35 years burial. When the enamel was chipped off this pipe, the perfect bond was shown by the fact that, when the coating was removed, the original mill markings on the steel pipe were clearly shown.

RESISTANCE TO SOIL CHEMICALS

Coal tar pitch is almost completely inert to moisture and soil chemicals. Coal tar coatings and coal tar pitch used as pipe coatings and for waterproofing have been dug up after 20-30 and 50 years of service underground. They were found to be practically unchanged. Coal tar pitch does not absorb any appreciable water and is not affected to any appreciable extent by soil bacteria.

The chemical stability of coal tar pitch is due to its aromatic character. The molecular unit of aromatic compounds is the benzene ring. It is a chemical structure of great strength and stability. In the symmetrical benzene ring, three single bonds and three double bonds resonate between the carbon atoms. These structures are called "aromatic rings", and the powerful inter-atomic forces holding them together account for the high stability of coal tar compounds. In the original formation of coal these benzene rings were chemicals united to make large, complex aromatic molecules. In the aromatic molecules comprising coal tar, the chemically inert carbon atoms outnumber hydrogen atoms two to one. It is the high aromatic content of coal tar - over 90% - that gives it great strength and resistance to attack by water or oxygen. Aromatic compounds, as a class of chemicals, have a markedly lower degree of water solubility and affinity for water than aliphatic compounds.

RESISTANCE TO SOLVENT ACTION

Coal tar enamels are substantially insoluble in petroleum products. For oil product lines, this is an important property. In the event of a leak in an oil line, the insolubility of the coal tar enamel coating will assure minimum damage to the coated pipe. This also applies to any pipeline or coated underground steel structure that is in contact with soil contaminated with petroleum products. A nearby foreign pipeline carrying crude or refined petroleum products can contaminate soil near a well-coated line.

RESISTANCE TO SOIL STRESS AND MECHANICAL DAMAGE

Pipe coatings must withstand a reasonable amount of mechanical abuse. If the proper grade of coal tar enamel is used for the conditions to which it must be exposed both prior to burial and after burial; and if it is used in accordance with manufacturer's instructions; and if it is used along with recommended shielding and also reinforcing where it is so specified; then coal tar enamels will not be distorted or damaged and the original coating thickness will be maintained, and the good service expected of a coal tar coating will be obtained.

RESISTANCE TO BACTERIA

Bacteria can feed on many hydrocarbon materials, but coal-tar coatings show no utilization by bacteria. Coal-tar enamel is inert to fungus attack. (13, 14).

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SPECIFICATIONS

TABLE 1

TESTS	METHOD	UN- PLASTICIZED	PARTIALLY PLASTICIZED	PLASTICIZED		
				Regular	AWWA	Hotline
Softening Point, R & B, F.	ASTM D 36	185 - 195	195 - 205	220-230	220 min.	250 min.
Penetration: 77 F-100 gms-5 sec 115 F-50 gms-5 sec	ASTM D 5	0 - 2 1 - 8	2 - 7 10 - 25	5 - 10 15 - 25	10 - 20 15 - 55	0 - 5 5 - 15
Filler (ash) %	ASTM D 271	22 - 32	22 - 32	22 - 32	25 - 35	22 - 32
Specific Gravity, 77F	ASTM D 71	140 - 160	140 - 160	140 - 160	140 - 160	140 - 160
PERFORMANCE TESTS						
High Temperature (1/16" max sag)	AWWA C 203	5 hrs @ 120 F	5 hrs @ 140 F	24 hrs @ 160 F	24 hrs @ 160 F	5 hrs @ 180 F
Low Temperature (no cracks)	AWWA C 203	5 hrs @ 30 F	5 hrs @ 0 F	6 hrs @ -20 F	6 hrs @ -20 F	6 hrs @ 0 F
Peel Test (no peel)	AWWA C 203	80-120 F	80-140 F	80-160 F	80-160 F	80-180 F
Spark Test 10,000 volts, low amperage, 2/32" coating tkns.	AWWA C 203	no sparks	no sparks	no sparks	no sparks	no sparks
Application Temp. (approx.) F.		400	450	475	475	500

TABLE 2

SYSTEMS	SHOT BLAST PRIMER 3/32" MIN ENAMEL GLASS WRAP 15 # ASBESTOS FELT 2/32" ENAMEL GLASS WRAP 15 # ASBESTOS FELT SEAL COAT OF ENAMEL 60 # KRAFT PAPER ELECTRICAL INSPECTION										SERVICE		
	1	2	3	4	5	6	7	8	9	10			
Single Coat Single Wrap	●	●	●		●						●	●	Normal Underground Environment
Single Coat Single Wrap	●	●	●	●							●	●	Normal Underground Environment
Single Coat Double Wrap	●	●	●	●	●						●	●	Normal Underground Environment
Double Coat Double Wrap	●	●	●	●	●	●					●	●	Severe Underground Environment - rocky terrain, corrosive soils, submarine lines, etc.
Double Coat Triple Wrap	●	●	●	●	●	●	●	●	●	●	●	●	Severest Corrosive Environment, such as river crossings, etc.

ELECTRICAL RESISTIVITY OF SPECIMENS OF ENAMELS

TABLE 3

Immersed in N/10 Sodium Chloride solution · Wheatstone Bridge, 100 V.

ENAMEL	RESISTIVITY IN MEGOHMS/SQ. FT.	
	30 DAYS	1 YEAR
Av. of 5 Asphalt Enamels	82,000	less than 0.6
Un-plasticized Coal Tar	200,000	over 200,000
Partially Plasticized Coal Tar	20,000	2,100
Plasticized Coal Tar, Regular Grade	6,000	1,300
Plasticized Coal Tar, Hotline Grade	8,000	1,900
Plasticized Coal Tar, AWWA Grade	1,600	300

FIGURE 1

RHEOLOGICAL DIAGRAM FROM BLUNT ROD PRESSURE DEFORMATION

Test Values at 77°F

Rate of Deformation
0.1 MM per Day

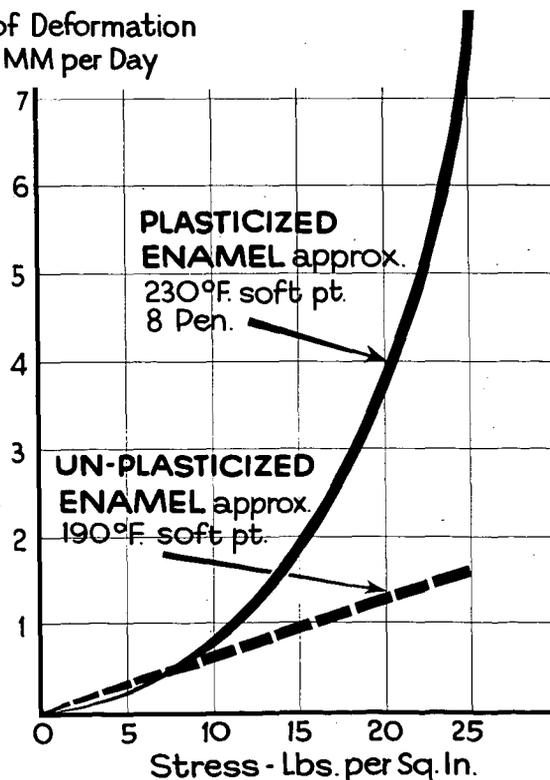


FIGURE 2

RHEOLOGICAL DIAGRAM FROM BLUNT ROD PRESSURE DEFORMATION

*Test Values
at 115°F*

Rate of Deformation
0.1 MM. per Hr.

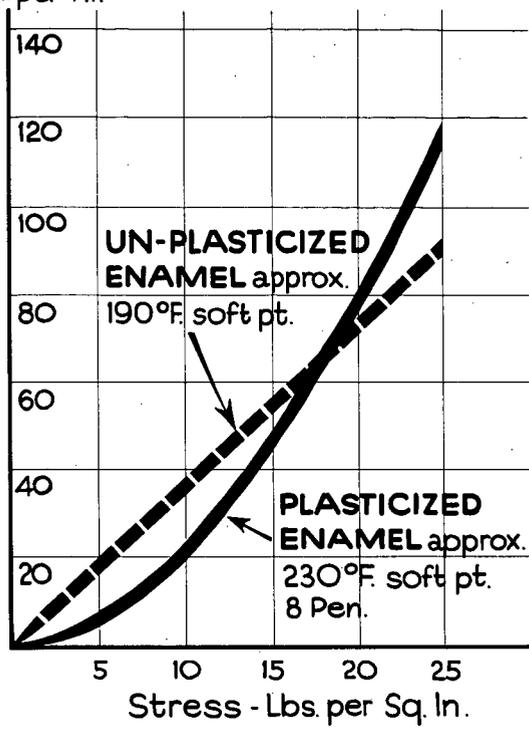
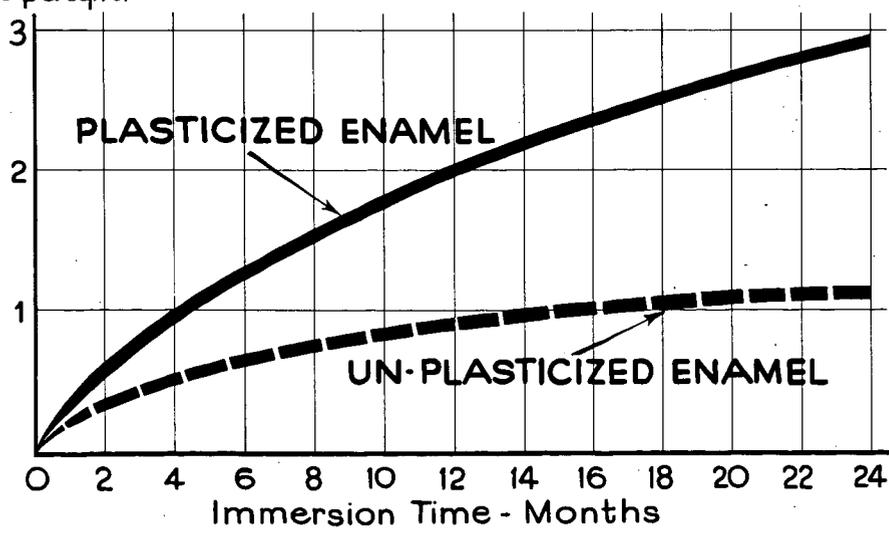


FIGURE 3

WATER ABSORPTION COAL-TAR ENAMELS

Absorption
GMS persq.ft.



CRITERIA FOR COMPOSITION AND
PROPERTIES OF HOT-APPLIED ASPHALT PIPELINE COATINGS

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Asphalt has been used to coat buried pipelines for many years. It was included in the API burial tests which were started in 1922 [1]. The asphalt coatings of that era were, for the most part, modifications of other products offered for pipe coating. During the last 20 years efforts have been directed toward producing asphalt base pipe coatings with the functional properties required of a coating in this specialized service.

To place this paper in proper context, it should be pointed out that corrosion mitigation on a buried pipeline nearly always involves a protection system. This protection system can consist of both a coating system and cathodic protection. The coating system can contain as many as four components, i.e. primer, hot-applied coating, embedded wrappers and outer wrappers. The first two coating components are the subject of this paper and the total protection system will be considered only as it affects the performance of these two asphaltic components.

The purpose of this paper is to review criteria for establishing composition and properties of asphaltic primers and coatings. New developments in prevention of disbonding through use of chemical additives will be presented. The total performance of a pipe coating system involves three separate use periods: application to the pipe, handling and storage of the pipe, and in-ground service of the pipe. Each of these use periods imposes functional requirements on the coating and exposes it to potentially deteriorating environments or forces. Both the functional requirement and resistance to deterioration must be considered in establishing criteria for coating properties.

Two important coating performance areas are retention of adhesion in the presence of cathodic protection and resistance to deformation by mechanical and soil stresses. These are the two performance areas which are treated in the most detail.

PROPERTIES OF HOT-APPLIED ASPHALT PIPE COATINGS

A long list of physical properties is used to describe hot-applied asphalt coatings. Some of the areas they describe are: 1] uniformity; 2] coverage rate; 3] application characteristics; 4] coating performance during pipe storage and handling; and 5] coating performance after the pipe is in service. Most of the properties now used to describe hot-applied asphalt coatings together with typical values are shown in Table I. Many of the test procedures are described by ASTM or some other specification writing agency. Those which are not so described appear in the appendix.

Broadly described, hot-applied asphalt coatings consist of an air-blown asphalt [75-85%] and a finely divided mineral filler [15-25%]. The mineral filler is used mainly to impart toughness. Most coatings on the market today fall within a 225 to 275° F softening point range and are quite hard [4-10 penetration at 77° F] at ambient temperatures.

The main function of the primer is to produce a strong adhesive bond. Therefore, they are formulated to have the low viscosities [70 centistokes at 77° F is typical] required for good wetting properties. Primers vary quite widely in composition. Solvent contents in the range of 55% by weight are needed to obtain the low viscosities. The film forming portion is usually mostly asphalt. Typical properties are shown in Table II.

Application Properties

Important application characteristics of a hot-applied pipe coating are:

1. Degree of change in composition and properties caused by heating and handling during application.
2. Fire hazard and fumes associated with its application.
3. Set time after application.
4. Its behavior during electrical inspection.

The thickness of coating applied to the pipe is largely dependent on the viscosity of the coating. Because of this, the coating's temperature-viscosity curve becomes an important consideration. In order to obtain thickness of $3/32$ " on the pipe, viscosities in the range of 100-200 centipoise are usually required. The temperature required to attain this viscosity varies from coating to coating. Thus, a coating's volatility, thermal stability, settlement ratio, and flash point should be considered in light of its temperature-viscosity curve.

Filler settlement ratio is a function of the viscosity of the fluid, density of the particle, diameter and shape of the particle. Since viscosity is set by the film thickness desired, the characteristics of the filler particle must be controlled to hold settlement to the desired level. The amount flash point exceeds application temperature is indicative of both fire hazard and fuming that can be expected. For practical reasons, electrical inspection voltages in the range of 25,000 are sometimes used. For a 50 mil. coating this is 500 volts per mil. of thickness. In order

to have a 2 to 1 safety factor, a coating should resist electrical breakdown up to 1000 volts per mil.

Handling and Storage Properties

Once a good coating application job has been achieved, what happens during the storage and handling period of the coated pipe determines the effectiveness of the coating when it is placed in service. The coating on stored pipe may experience temperatures as low as 0° F during the winter in northern climates and as high as 160° F when exposed to the sun during the summer in southern climates. A 100° F drop in surface temperature within 24 hours can be experienced in a given location. A coating must be able to relieve the shrinkage stresses developed during this cooling, otherwise it will crack. The low temperature crack test is used as an indicator of performance in this area. The impact test is used as a measure of mechanical abuse coated pipe can withstand in handling without film fracture. The sag test is used as an indicator of resistance to flow when exposed to summer sun in southern climates.

In-Service Performance Properties

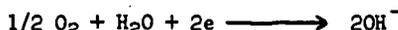
Now let us consider the properties that are indicative of a pipe coating's performance in service. Some of these are: 1] cathodic disbonding resistance; 2] flow resistance; 3] low temperature crack resistance; 4] electrical resistance; and 5] water absorption. The relative importance of each of these varies widely from one installation to another. For example, cathodic disbonding resistance of a coating is of little

importance unless the pipe is cathodically protected. The importance of flow resistance is related to the nature of the soil surrounding the pipe and to the pipeline operating temperatures.

Cathodic Protection

Since cathodic protection is widely used to complement coatings on buried structures, it is important to consider their efficiency as used together and the effect of one upon the other. Cathodic protection involves impressing a negative potential on the structure to be protected. The protected structure thus becomes the cathode of a large electro-chemical cell. Some of the chemical reactions that are promoted by its negative character are:

In aerated nearly neutral soils oxygen reduction can occur:



In acid soils the hydrogen ion is reduced:



Because the hydrogen ion has such a great affinity for H_2O [2]

the more complete picture is:



This is the primary reaction occurring in neutral and alkaline soils also. The H^+ ion becomes available from ionization of H_2O . Since it has a more noble position in the electromotive series than other cations usually present, it is preferentially reduced. Depletion of H^+ concentration at the cathode surface produces additional H_2O ionization. The over-all result is the formation of H_2 gas at the cathode and an ever increasing OH^- concentration in its vicinity. Some of the metal cations precipitate as hydroxides. Others react further such as with CO_2 to precipitate as carbonates.

The effect of cathodic protection on loss of coating adhesion has been considered by others [2,3,4]. Since the use of cathodic protection in conjunction with a coating is based on the premise that it should protect the metal at coating imperfections, our laboratory investigations employ specimens with intentional "holidays" [holes in the coating]. The two procedures used are described in the Appendix. The short-term test is usually run seven days and is used as a screening test. The long-term test is run from 30 to 270 days.

Figure 1 is illustrative of a good and poor performing coating system in the short-term test. Usually there is loss of coating bond with no apparent displacement of the coating by hydrogen. Occasionally slight displacement is noticed. On one occasion a coating system disbonded completely and hydrogen pressure lifted it approximately 1/4" from the panel surface at the center. The extension was by cold flow without rupture of the coating. This is illustrated in Figure 2. Pictures illustrating a good and poor performing system in a 270-day cathodic disbonding test are shown in Figure 3. [All photographs were taken after disbonded coating was mechanically removed.]

Current drain to the test specimen is rather irregular and often does not correlate with the amount of disbonding. A graph illustrating the order of magnitude of current drain for three coatings that showed different degrees of disbonding is shown in Figure 4.

The use of additives in the primer for improving the cathodic disbonding resistance of a poor performing primer-coating system was investigated. The additives were used at a concentration of 1% by weight. Additives

which improved resistance to cathodic disbonding included an imidazolium chloride [7,8], an amine [9], and a substituted pyridine [10]. Disbonding resistance was reduced by three diamines and two commercial anti-strip additives [adhesion improvers for road asphalts]. A listing of materials tested and results obtained are shown in Table III.

Our work shows that cathodic disbonding is affected both by the primer and the coating used over it. However, as would be expected the primer is the most important component in controlling this property. Data to illustrate this is shown in Table IV. Cathodic disbonding can be cut in half by going from a poor to good performing coating and can be cut ten fold by going from a poor to good performing primer.

Flow Properties

A buried pipe coating is subjected to the pressures caused by the weight of pipe and its contents and to pressures generated by expanding and contracting soil. If it flows under these pressures, the pipe is no longer uniformly coated. A blunt rod deformation test is widely used to rate flow resistance of pipe coatings. This test consists of measuring the deformation [in 0.001 inches] at given time periods caused by the weight of a stainless steel rod 1/4" in diameter and of such length as to produce a pressure of 2 psi. A plot of values obtained in this test vs. penetration [both at 150°F] is shown in Figure 5. There is very little correlation. Both measure flow resistance but at greatly different rates of shear. For this reason these two tests would give proportional values only for those bituminous compositions of equivalent shear susceptibility.

Since loading is lower [lower shear rate] in the rod deformation test, it will give lower values with increasing shear susceptibility for materials of equivalent penetration at the temperature under consideration.

Water Absorption and Electrical Properties

Water absorption and electrical properties [5] of asphalt is discussed in detail by the authors in a recently issued book edited by Hoiberg. Some important points related to this subject are:

1. Pure asphalt absorbs water at a very slow rate
2. The prime consideration is whether or not the physical nature of a pipe coating is materially changed by the amount of absorption which occurs.
3. Electrical resistance is reduced by water absorption but even for high absorbers current drain through the coating would be quite small on a cathodically protected pipeline [6].

SUMMARY

In assessing the performance of a pipeline coating, three time periods during its utilization must be considered. These are: 1] its application to the pipe; 2] the pipe storage and handling period; and 3] the pipeline in service period. The latter period is the one of major importance but a coating's usefulness during this period is greatly affected by its behavior in the first two. Cathodic protection is widely used as a complementary means of corrosion mitigation on buried structures and its disbonding effect on coatings is an important consideration.

Cathodic disbonding is affected by composition changes in both the primer and the hot-applied coating. It is most sensitive, however, to changes in the primer. The flow properties of hot-applied asphalt coatings are an important factor in their performance. It is possible to have materials varying widely in shear susceptibility, therefore, meaningful laboratory tests must employ loading rates of the same magnitude and at the same temperature that will be encountered in service.

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APPENDIX

TEST PROCEDURES FOR HOT-APPLIED ASPHALT PIPE COATINGS

CATHODIC DISBONDING TESTS

I. Preparation of Electrolyte for Cathodic Disbonding Tests

The synthetic sea water used as the electrolyte in the disbonding test conforms to military specification MIL-L-21260 and has the following composition:

<u>Ingredients</u>	<u>g./l. of H₂O</u>
Magnesium Chloride - 6H ₂ O	11.0
Anhydrous Calcium Chloride	1.2
Anhydrous Sodium Sulfate	4.0
Sodium Chloride	25.0

The pH of the solution shall be adjusted to a value of 8.0 to 8.2 by addition of a 5% solution of sodium carbonate or a 5% solution of hydrochloric acid, whichever is necessary. All chemicals used should conform to ACS standards for analytical reagents chemicals.

II. Preparation of Test Specimens for Short-Term Cathodic Disbonding Test

A. Introduction: The following is the standard procedure for preparation of specimens for short term cathodic disbonding tests. Specimens are prepared from 2-3/4" x 5-7/8" x 0.035" open hearth steel panels.

B. Preparation - Procedure:

1. First day - Metal surface preparation and application of prime coat.
 - a. Wipe panels free of oil.
 - b. Slush panels in nearly boiling 300/360 b.r. naphtha.
 - c. Sandblast both sides of panel. For blasting, a sharp, dry sand having a minimum of 50% retained on a No. 60 sieve shall be used with an air pressure of not less than 50 pounds per square inch.
 - d. Solder copper lead wire to panel using rosin core solder.
 - e. Brush free sand from panel with stiff brush.
 - f. Apply primer to panel using clean brush for each primer.
 - g. Allow panels to dry overnight.

At all times during the above procedure precautions should be taken to prevent contamination of test side of panel. The test side of the panel is designated as the side opposite the soldered wire. The primed panel should not be allowed to stand for more than 24 hours before application of hot enamel.

2. Second day - Application of hot enamel.

- a. Apply hot enamel to test side of panel to a thickness of 55/65 mils, using a plaqueing machine.
- b. Incline panels on 3 oz. ointment cans with coated side down and flow coat back side of panel with hot enamel.

- c. Dip all edges of coated test specimens in hot enamel to prevent accidental damage at weak points. Cool panels in ice water immediately after dipping to prevent "running" of the enamel.
- d. Drill a 1/16" "holiday" through the coating on the test side of the prepared test specimen.

Care must be exercised in coating the test side of the primed panel with hot enamel. The coating must be in the 55/65 mil range, otherwise reproducibility of the test will be affected.

III. Preparation of Test Specimens for Long-Term Cathodic Disbonding Test

A. Introduction: The following is the standard procedure for preparation of specimens for long-term cathodic disbonding tests. Specimens are prepared from 2' lengths of 2" I.D. steel pipe threaded on each end to receive a plastic coupling on one end and a plastic cap on the other.

B. Preparation - Procedure:

1. First day - Metal surface preparation and application of prime coat.
 - a. Solder copper lead wire to inside of pipe.
 - b. Sandblast pipe surface using a sharp, dry sand having a minimum of 50% retained on a No. 60 sieve shall be used with an air pressure of not less than 50 pounds per square inch.
 - c. Brush free sand from sandblasted pipe using stiff brush.
 - d. Apply primer to pipe using clean brush for each primer.
 - e. Allow pipes to dry overnight.

At all times during the above procedure precautions should be taken to prevent contamination of freshly sandblasted pipe surface. The primed pipe should not be allowed to stand for more than 24 hours before application of hot enamel.

2. Second day - Application of hot enamel.
 - a. Screw the coupling and cap to their respective ends of the pipe.
 - b. While pipe is mounted horizontally and rotating at a constant speed, flow coat with hot enamel to a thickness of 90 + 5 mils. Bring hot enamel up over plastic coupling and cap on each end.

- c. After coating has cooled, dip capped end of pipe into molten enamel to effect a water-tight seal.
- d. Drill four 1/16" dia. holidays in the coating equidistant apart and offset 90° from each other along the pipe length.

IV. Operation of Test Apparatus

- A. Test Apparatus: The attached Figure I describes a single cathodic disbonding test circuit and the equipment used for measuring potential and current drain. Sixty 100 ohm rheostats and insertion jacks are mounted on a central panel board and connected in parallel to a single anode. Use of a phone plug enables taking current and voltage readings without interrupting current drain to the test specimen. The constant voltage transformer may be dispensed with if an unvarying source of a.c. is available.
- B. Test Procedure: The test specimens prepared as described above are immersed in the solution of synthetic sea water around an anode and subjected to a potential of -1.50 volts with reference to a saturated calomel electrode. Current readings are made and recorded, and the voltage is adjusted to -1.50 volts weekly on each specimen. Any addition of water to compensate for evaporative losses and necessary pH adjustments are also made at this time. The equipment used in the cathodic disbonding test is illustrated in Figure 1.

At the end of the prescribed test period the specimen is removed from the bath and examined for disbonding beyond the intentional damage. The loosened coating is removed to the point where firm bond still exists. The disbonded area is then measured and recorded in square inches.

High Temperature Sag Test

Preparation of test plates: Test plates shall be mild steel of 12" x 4" x 3/16" size. One side of each plate shall be freshly sand-blasted to a uniform steel gray surface, completely removing stains, rust and mill scale.

For blasting, a sharp, dry sand having a minimum of 50% retained on a No. 60 sieve shall be used with an air pressure of not less than 50 pounds per square inch.

Application of the coating: The plates shall be primed with the recommended primer for the coating under test. After the primer has cured as recommended by the manufacturer. The molten hot coating shall be applied by pouring on the plates supported at an incline of 10 degrees. Temperature of the coating shall be adjusted to obtain a film thickness of $3/32" \pm 1/64"$.

Test procedure: Reference lines drawn with wax pencil or chalk shall be drawn at three-inch intervals parallel to the 4" side. The coated plates shall then be placed vertically in a test oven with the scribed lines horizontal at the desired test temperature for the desired length of time. The oven shall be capable of controlling within $\pm 5^\circ$ F of the test temperature.

After completion of the test the plates shall be removed from the oven and allowed to cool to room temperature. The lowest point on each of the lines shall be checked against the reference point on the edge of the plate and the difference reported as sag distance.

Low Temperature Crack Test

Preparation of test plates: Same as for High Temperature Sag Test.

Application of Coating: Same as for High Temperature Sag Test.

Test Procedure: Place the coated plates in an air bath capable of controlling at the desired test temperature $+ 5^\circ$ F. After a period of 6 hours at test temperature, remove the plates and allow them to warm to room temperature and examine for evidence of cracking or disbonding. A jump spark holiday detector may be used to examine for cracking.

Resistivity, Ohm-cm.

Scope: This procedure is intended for determining the volume resistivity of pipe coating materials having values up to 10^{17} ohm-cm. It is intended only for those materials capable of being formed in films and sufficiently hard to be handled at 75° F without damage.

Equipment: Film former - Carver Press equipped with heated platens
240 Regulated High Voltage Power Supply -
Keithley Instruments, Cleveland, Ohio
6105 Resistivity Chamber - Keithley Instruments
Decade Shunt - Model 2008 Keithley Instruments
Ammeter - 0-10 scale - Hooked through decade shunt -
Keithley Instruments.

Procedure: A. Initial resistivity

Films, 50-70 mils thick, are formed by a suitable means, e.g. Carver Press. Hot forming of the films between Teflon Paper will enable easy release. Circular test specimens, 3 inches in diameter, are then cut from the films. Measure and record the specimen thickness in cm.

Place the test specimens between the electrodes in the resistivity chamber and impress a 500-volt potential across the film. Wait 10 minutes to allow the current across the film to equilibrate and note the amperage.

Using Ohm's Law, calculate the film resistance:

$$E = IR$$

Where: E = potential across film, volts
I = current drain across film, amps.
R = resistance of film, ohms

The value for R is then inserted in the volume resistivity equation:

$$P = \frac{RA}{L}$$

Where: P = volume resistivity of film, ohm-cm.
R = film resistance, ohms
A = area of electrode face, cm.²
L = film thickness, cm.

B. Resistivity after immersion:

Immerse the test specimens in distilled water for the desired length of time. After such time, remove the specimens, pat dry with an absorbent tissue, and allow to air dry for one hour. After one hour proceed with the volume resistivity determination outlined above.

Voltage Breakdown

Coating is applied to a steel plate such that coating thickness of 5 to 10 mils is obtained. Voltages greater than 1000 times the film thickness in mils is applied across the coating with an electric holiday detector equipped with a variable voltage regulator.

Water Absorption

Test panels are prepared by pouring the molten enamel down the inclined face, at approximately 30° from the horizontal, of the polished aluminum test panels, each 2-3/4" x 5-7/8" of 20 gauge metal. By balancing the inclination of the panel and the temperature of the coating against the viscosity of the test material, test films of 90 to 100 mils thickness can be obtained on both sides of the panel. After cooling, the edges of the coating are trimmed at an angle of 45° and the edges then coated uniformly by hand dipping in the enamel. The panels are weighed initially and again after 35 weeks' immersion in water, the water absorption being reported as percentage by weight of initial weight of film.

TABLE I

HOT-APPLIED ASPHALT PIPE COATINGS
TYPICAL PROPERTIES AND THEIR SIGNIFICANCE

Property Information is use for:	Property	Typical Value
Indicating Application Characteristics	Flash Point, ASTM D-92	575+
	Temperature-Viscosity curve, Brookfield viscometer	---
	Voltage breakdown resistance, volts per mil ¹	1000+
	Penetration at 150°F, ASTM D-5	30
Indicating Coated Pipe Handling and Storage Characteristics	Settlement ratio [filler], AASHTO T 109-42 [modified]	1.10 at 400°F
	Flow resistance [rod deformation], Asphalt Institute ²	15 mils, 6 hrs., 115°F Pass to 0°F 160°F ⁴ Pass to 32°F
Indicating Coating Performance in Service	Low temperature crack resistance, Asphalt Institute ³	15 mils, 6 hrs., 115°F
	High temperature sag resistance, Asphalt Institute ³	Pass to 0°F
	Impact resistance, [Southern California Gas Company procedure [modified]]	0.03-0.5 7-day test ⁴ 1 x 10 ¹⁵ +
	Flow resistance [rod deformation], Asphalt Institute ²	1.0 in 35 weeks
Indicating Uniformity	Electrical resistance, ohm-cm ¹	7
	Water absorption, wt. percent ¹	240
	Penetration at 77°F, ASTM D-5	20
Determining coverage rate per unit of weight	Softening point, ASTM D-36	10
	Ash [mineral filler], wt.%, ASTM D-482 [modified] Weight, pounds per gallon, ASTM D-71	10
Weight, pounds per gallon, ASTM D-71		10

¹Test procedure given in the appendix

²Asphalt Protective Coatings for pipe lines, C.S. No. 96, 2nd edition, The Asphalt Institute, Dec. 1958

³Asphalt Protective Coatings for pipe lines, C.S. No. 96, The Asphalt Institute, May 1954, now superseded. Test procedure given in the appendix.

⁴This property is quite dependent upon the primer used.

TABLE II

PRIMER FOR HOT-APPLIED ASPHALT
PIPE COATING - TYPICAL PROPERTIES

<u>Property</u>	<u>Typical Value</u>
Flash Point, T. O. C., ° F	95
Viscosity, centistokes at 77° F	70
Solids Content, wt. %	45

TABLE IV

RELATIVE EFFECT OF COATING
AND PRIMER ON CATHODIC DISBONDING

<u>Primer</u>	<u>Coating</u>	<u>Disbonded area 7 days, -1.5 volts, sq. in.</u>
I [poor]	A [poor]	0.52
I [poor]	B [good]	0.26
II [good]	A [poor]	0.04
II [good]	B [good]	0.03

TABLE III

EFFECT OF ADDITIVES TO PRIMER ON SEVEN-DAY CATHODIC DISBONDING

[Additive used at 1% by weight, Voltage - 1.5 to sat. cal. electrode]

Trade Name	Additive Compound Type	Disbonding		
		Area, in. ² Primer + Additive	Area, in. ² Primer [Control]	Ratio, Additive Primer/ Control
Nalquat G-8-13	1,[2-Hydroxyethyl]- 2-heptadecenyl, 1-benxyl- 2-imidazolinium chloride	0.332	0.695	0.478
Armeen C	Coco amine	0.313	0.441	0.705
Duomeen S	Soya, 1,3-propylene diamine	1.92	0.609	3.16
Duomeen T	Tallow, 1,3-propylene diamine	1.15	0.490	2.35
Ethoduomeen T12	Alkoxyated alkyl 1,3-propylene diamine	2.78	0.706	3.93
PAP 250	Polyalkyl pyridine	0.397	0.554	0.715
Nalclad RL-1	Commercial anti-strip additive	0.92	0.410	2.24
Pave	Commercial anti-strip additive	1.42	0.465	3.05

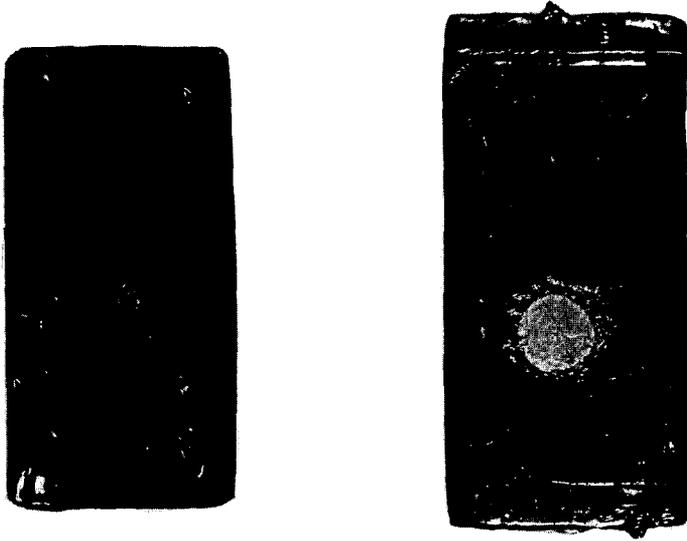


FIGURE 1

GOOD AND POOR PERFORMING COATING SYSTEMS
IN A 7-DAY CATHODIC DISBONDING TEST

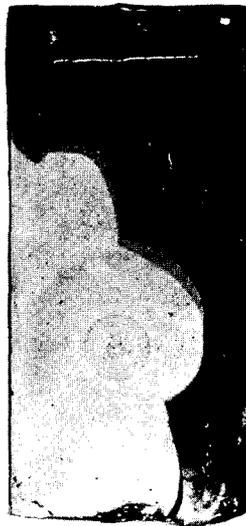
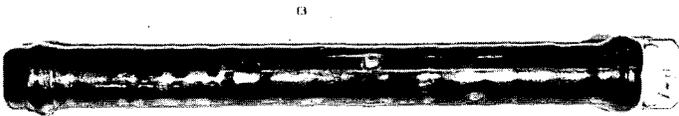


FIGURE 2

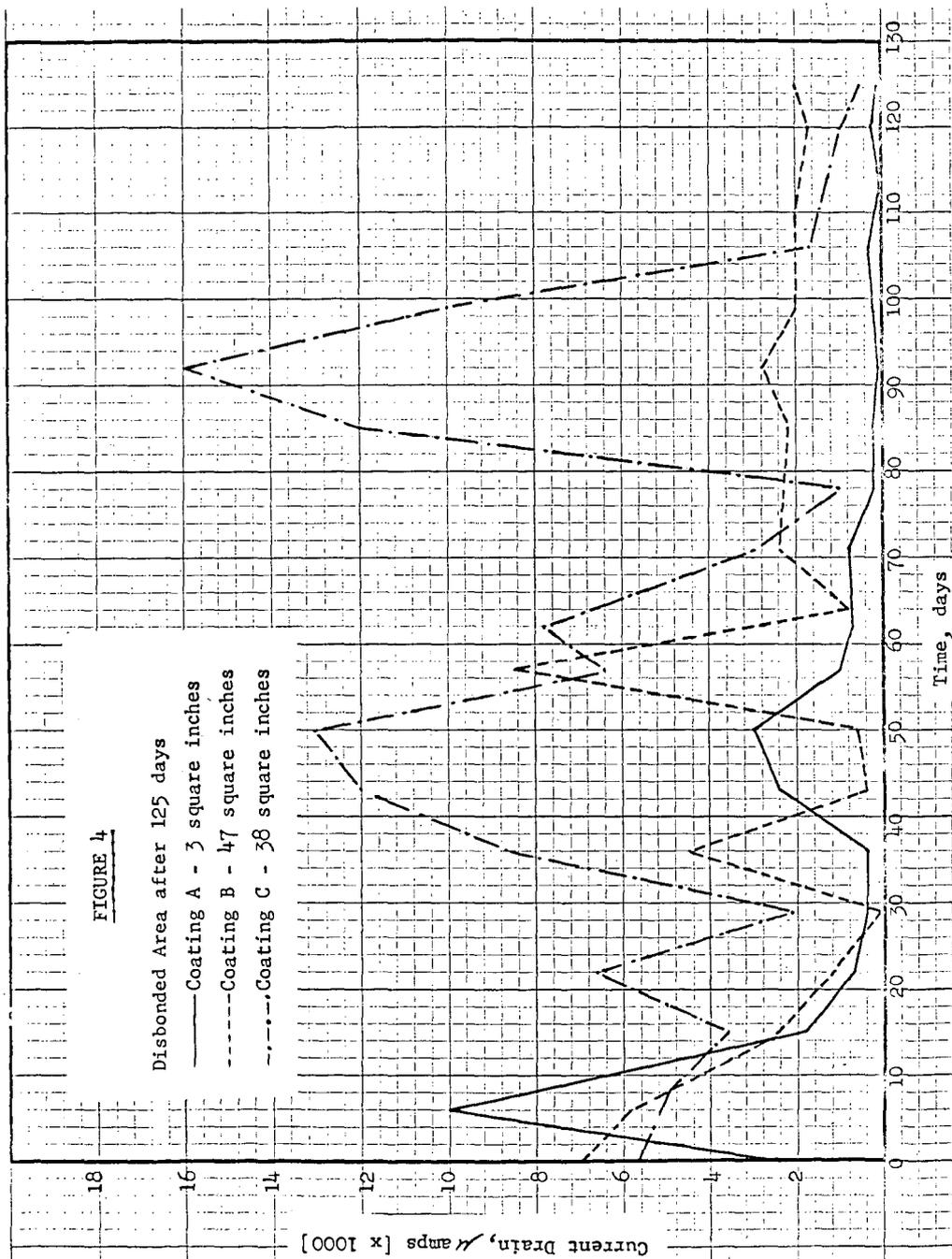
COATING COLD FLOW FROM HYDROGEN PRESSURE
IN CATHODIC DISBONDING TEST

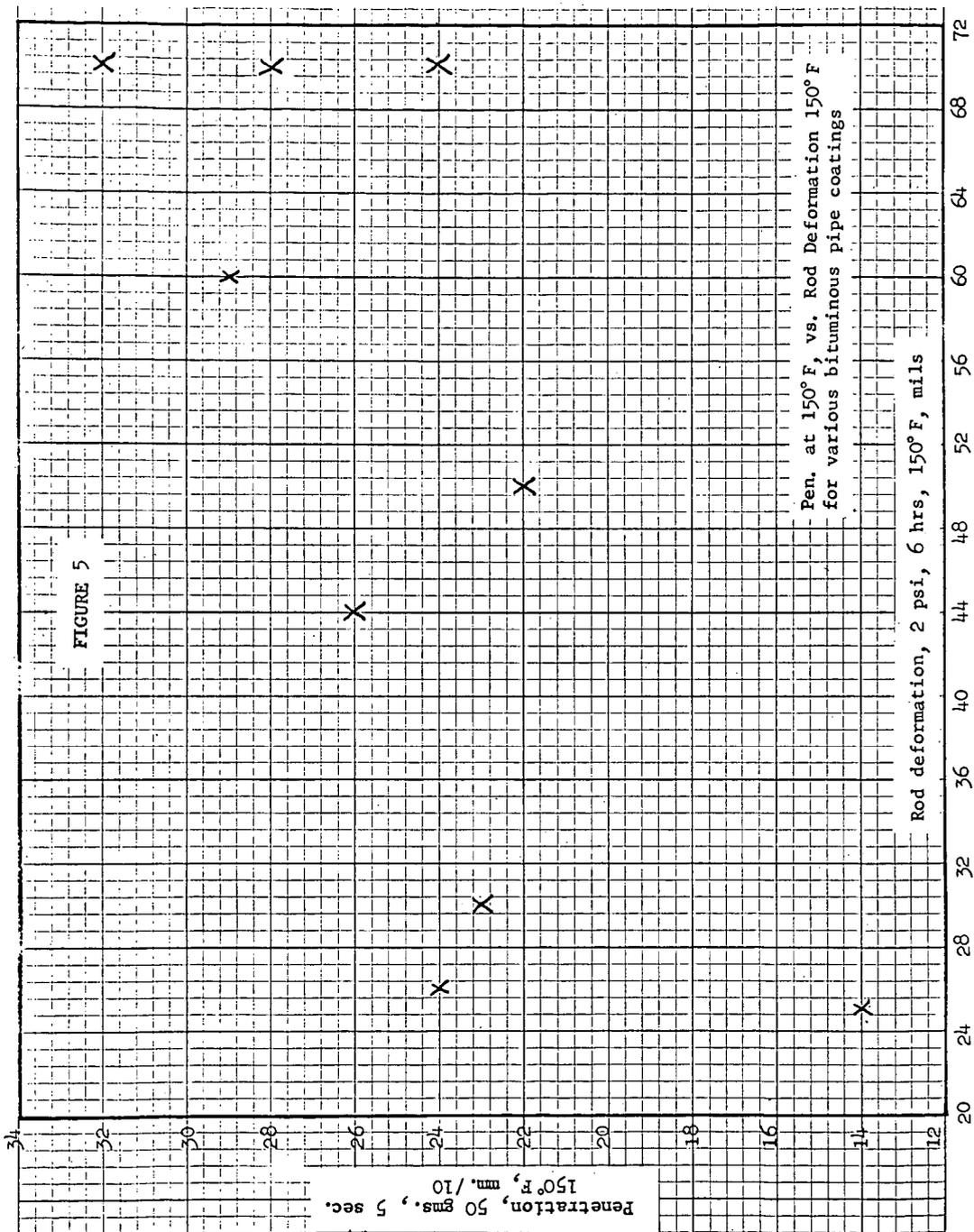


3-2-1

FIGURE 3

GOOD AND POOR PERFORMING COATING SYSTEMS
IN A 270-DAY CATHODIC DISBONDING TEST





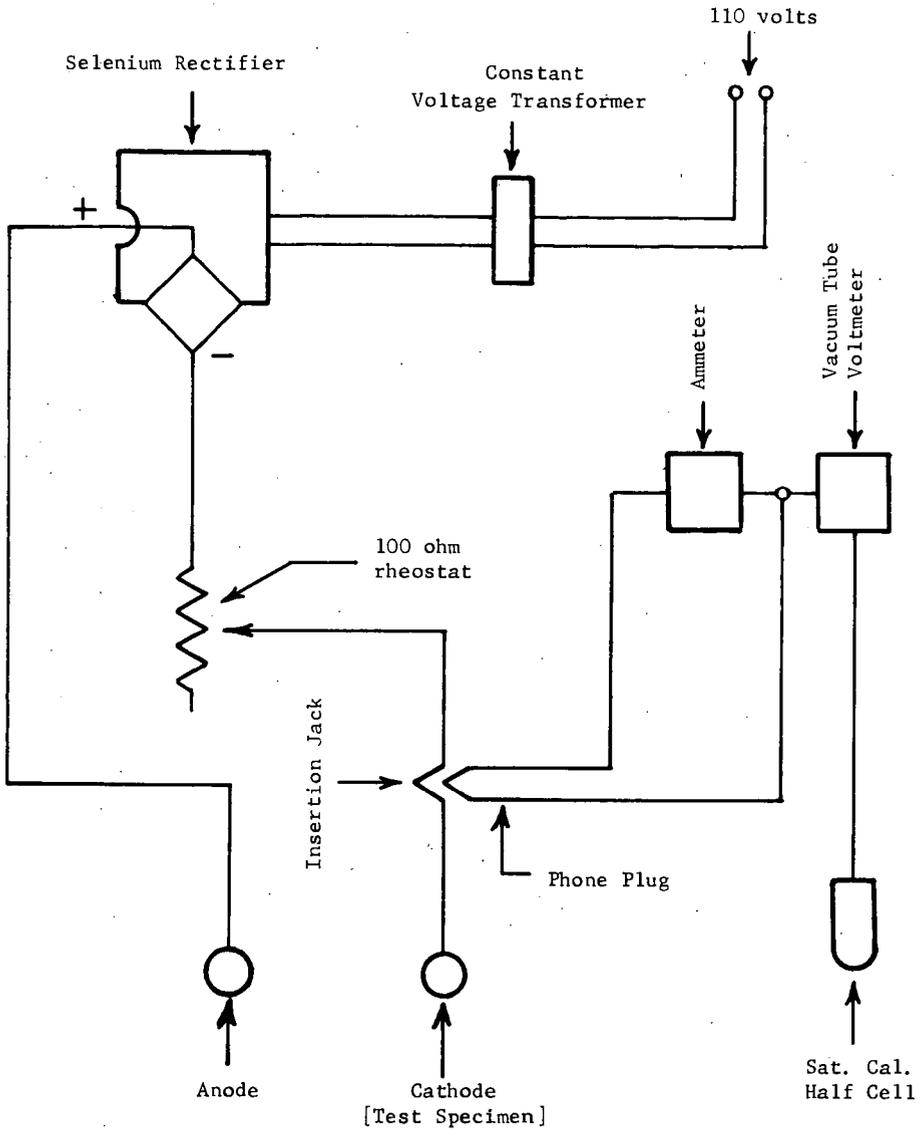


FIGURE I - APPENDIX

COLD APPLIED COAL TAR PAINTS

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Coal tar and coal tar pitch base coatings probably date back to the first production of these black viscous materials in gas plants and by-product coke ovens. It can safely be said that historically they have been manufactured and used for at least one hundred years. Early in their production they found wide use as water or moisture proofing paints and so even today we find them specified frequently by the marine and water works industries.

Tar and pitch are sticky materials which when compounded into paints show excellent wetting and adhesive properties over all types of surfaces and while sand or grit blasted substrates give the best results, a considerable degree of protection is still obtained with the tar paints over tight mill scale and wire brushed steel.

Tar paints are not recommended for severe chemical exposures, but they are inert enough to withstand most soil acid and alkali concentrations in underground installations and salt conditions encountered aboveground, in shore installations, fertilizer plants and sewerage works.

Coal tar paints and coatings, like other systems have limitations which can be pointed out here before discussing their general composition. First, they, like the old Ford cars, come in only one color - black. It is extremely difficult to pigment or dye a coal tar paint to get any other color with one exception. The exception is an aluminum color which can be obtained by incorporating about 1.5 pounds of leafing aluminum powder to a gallon of paint. The coal tar paints cannot usually be overcoated with a colored topcoat without bleed through nor for that matter can they be used as a topcoat over old paints without softening and wrinkling of the undercoat.

One other aesthetic consideration is that of alligating. Most coal tar paints alligator severely in sunlight exposure, but in many cases no bare metal is exposed and the moisture barrier is still performing successfully after years of exposure. One other objection sometimes encountered is that the coal tars have a rather sharp and strong odor.

In all of the above, the cut-back or solvent-type coal tar paints have been referred to. There is one coal tar coating which has fewer of these handicaps and that is the so-called coal tar emulsion which will be discussed later.

Classification of Coal Tar Paints

There are perhaps hundreds of proprietary formulations in which coal tar or coal tar pitch has been used either as a major or minor component with varying degrees of success. The voluminous patent literature attests to this, but here I would like to limit the classification shown below to the few products which have attained a fairly high volume of commercial use over the past fifty years and are still marketed by the four or five major tar processors. Where possible, an applicable published specification is included which will serve as a guide to the general composition of the coating rather than trying to list the limitless minor modifications, some of which are unpublished and unknown to the author, of the various manufacturers.

1) Refined Coal Tar

Under this classification are road tars of various consistencies and while in the broad sense they may be considered coatings, they are in general beyond the scope of this paper. The basic coal tar vehicle is included here, however, because it is a logical starting point and occasionally it is specified as an ingredient for, say, an anti-fouling coating, an asbestos-filled coating or caulking compound, or more recently as the coal tar component of a tar-epoxy system. Published tar specifications are as follows:

- a) ASTM - Standard Specifications for Tar - ASTM-D490-47
- b) Federal - Road Tar #R-T-143, 1940
- c) AASHO - American Association of State Highway Officials
#M52-42
- d) MIL-T-15194 (Ships) May 1950 Tar, Coal - This specification covers coal tar to be used as an ingredient for ship bottom paints and lists the following requirements:

Specific Gravity at 25°C.	-	1.14 to 1.24
Water	-	1% Maximum
Carbon Content (Free)	-	15% Maximum
Ash	-	0.5% Maximum
Viscosity, Engler		
Specific at 50°C.	-	15 - 35

2) Coal Tar Pitch - Solvent Cutbacks

These coal tar paints are similar to a varnish and are manufactured of coal tar pitch and solvent to a brushing consistency. They can be applied by brush, spray or roller much as any other paint. Coverage rates are normally about 400 square feet per gallon, giving a dried film thickness of about 2 mils per coat. Two to three coats are usually specified. There are two types, a) a general maintenance paint made with a heavy coal tar naphtha solvent and b) a potable water tank paint made with a highly refined solvent (xylene) to reduce residual odor and taste. Specifications are as follows:

Coal Tar Pitch Base Paints

	<u>Type a</u>	<u>Type b</u>
	<u>Military Spec. No.</u>	<u>American Water Works Association</u>
	MIL-P-6883 Aug.1950	AWWA D 102-62 T
	<u>Supersedes AN-P-31a</u>	<u>Sec. 3.11</u>
Color	Jet Black	-
Specific Gravity at 25°C.	1.07 to 1.12	-
Weight per Gallon, Lbs.	-	8.7 to 9.7
Viscosity at 25°C.	1 to 1.5 poises	60 - 75 sec. (Stormer)
Flash Point	95°F. Min.	70°F. Min.
Moisture, %	.05 Max.	-
Acid No.	3.0 Max.	-
Ash, % by Wt.	0.5 Max.	0.5 Max.
Non-Volatile, % by Wt.	53 Min.	-
Softening Pt. of Non-Volatile	55 - 65°C.	-
Free Carbon, % by Wt.	15 Max.	-
Unsaponifiable, % by Wt.	99.5 Min.	-
Volatiles, to 140°C.		
Wt. %	None	-
To 200°C. Wt. %	-	45 Max.
140 to 235°C., Wt. %	43 Max.	-
Drying	High Gloss	After 24 hours at 77°F. and flushing shall impart no objectionable taste or odor to water
	1 Hr. to Touch	Shall contain no added filler, pigments, fibrous materials or asphalt.
	8 Hrs. to Handle	
With Aluminum Powder	1.3#/Gallon	

3) Medium Bodied Coal Tar Paints

These intermediate coal tar paints contain mineral filler as well as pitch and solvent and are used where corrosive conditions require a heavier coating film than that obtainable with the varnish-type coatings.

They are somewhat easier to apply than the heavy bodied coatings and are often more successfully used on concrete with little or no tendency to mud-crack. Normal coverage is about 150 - 200 square feet per gallon which gives about 6 to 8 mils dry film per coat. Two coats are generally specified.

To the author's knowledge there are no Government specifications for this coating but it is believed that the following characteristics will describe their general composition:

Medium Bodied Coal Tar Paints

Weight per Gallon	10.5 - 11.5 Lbs.
Consistency	Viscous - (40 poises or more)
Moisture	1.0% Max.
Per Cent Solids	70 - 80
Filler (Ash), %	15 - 25
Volatiles to 235°C., %	20 - 30
Flash Point	95°F. Min.
Drying Time Between Coats	Overnight

4) Heavy Bodied Coal Tar Coatings

Of all the cold applied coal tar coatings, the one that is most widely known and used is the thixotropic heavy bodied paint made from processed or plasticized pitch, solvent and mineral fillers. By plasticized pitch is meant the more highly flexible material which is made by incorporating pulverized coal, heavy oils and pitch in a special high temperature processing operation. The coal appears to be suspended in a matrix of oil and pitch in a colloidal state, yielding high melting points but none of the brittleness associated with the straight distilled coal tar pitch. When this pitch is cut back with solvent, and put through a colloid mill a highly thixotropic coating material is obtained. After standing a day or so, the material in the container appears to be solid - in fact the can can be tipped upside down without causing the material to flow out. On dipping a stirring rod into it, it has the consistency (100 poises or more) of black mayonnaise which breaks down on vigorous stirring to a suitable application consistency.

This coating is applied without thinning, by brush, roller or heavy duty spray equipment at a coverage rate of 50 to 70 square feet per gallon and gives a dry film thickness of 15 to 20 mils per coat which will not sag from a vertical surface while wet. Two coats are normally specified. It is used on marine piling and other steel structures in wet environments such as underground piping and penstocks, and on cement, masonry, and galvanized steel, in pickling plants, sewerage and water works and chemical plants as a heavy duty maintenance paint.

In normal application thickness (35 mils in two coats) the coating remains flexible for years either submerged or underground. However, it does tend to embrittle in sunlight exposure and to overcome this a final coat of a tar-emulsion is often used.

The coating, being so widely used, has many published specifications, some of which are:

- Bureau of Reclamation - Spec. No. CA-50, Oct. 1956
- Navy - Bureau of Yards & Docks - Spec. No. 34 yd, May 1963
- Steel Structures Painting Council - Spec. No. PS 10.02 64 T, July 1964
- Military - Docks - Spec. No. MIL-C-18480A, Oct. 1961
- American Water Works Assoc. - Spec. No. AWWA C-203-62 Sec. 2.10

The Military Specification is fairly representative and often referred to, so the requirements shown there will act as a reliable guide as to the composition of the heavy bodied coal tar paint. They are shown as follows:

Coating Compound - Coal Tar Base
Spec. No. MIL-C-18480A Docks October 1961

Specific Gravity (77°F.)	1.2 - 1.5
Flash Point	95°F. Min.
Ash, % by Wt.	15 - 25
Water, % by Wt.	1.0 Max.
Distillate, % by Wt.	
To 150°C.	0
To 235°C.	18 - 30%
Asphalt	None
Free Carbon, %	5 - 25
Softening Point of Residue, R&B	205 - 240°F.
Penetration of Residue, 100 g., 5 sec., 77°F.	5 Min.
Coverage	55 - 70 sq.ft./gal.
Dry to Touch	6 Hrs.
Dry for Recoating	24 Hrs.

5) Coal Tar Emulsions

Coal tar pitch and water dispersions or emulsions form interesting coating systems whose properties are distinctly different from any of the previously mentioned solvent cutbacks. In the first place, water is the external or continuous phase so they may be diluted with water (not usually recommended) and clean up of equipment is facilitated. The emulsifying agent is usually a Bentonite clay and the pitch used is fairly soft, 50°C. R&B or lower. On drying, the soft pitch absorbs some of the clay forming a lattice-like structure which does not re-emulsify when wet, will not run or alligator in direct sunlight and is fairly flame resistant. The flexible dry films will withstand wide temperature fluctuations (minus 50°F. to over 180°F.) without becoming brittle or sagging. The coating, however, does reabsorb some water when immersed, so it is seldom used or specified for underwater or underground service. Its main use has been as a topcoat over other bituminous systems to prevent embrittlement and improve weathering properties. It in turn can be topcoated with aluminum or other fast drying color coats because the clay prevents the bleed-out so often encountered with coal tar paints.

The coal tar emulsion is also the common driveway and pavement sealer recommended for asphalt or tar macadam surfaces where resistance to gasoline spillage is required. One precaution in the use of the emulsion is that it should not be applied if rain or freezing conditions are anticipated before it has dried. Coverage is normally 50 to 60 square feet per gallon giving a 10 to 15 mil dry film thickness per coat.

Recently a combination rubber latex/coal tar emulsion has appeared on the market and claims are made that it is much tougher and more ductile than the straight coal tar emulsion. Other properties are similar.

There are two published specifications for the coal tar emulsion which are fairly descriptive of the coating composition. These are (1) Federal #R-P-00355a (GSA-F.S.S. dated October 16, 1957) and (2) Military Specification No. MIL-C-15203c (Ships) dated November 1959. Requirements of the latter are:

MIL-C-15203c (Ships)
Coating Compound-Bituminous Emulsion

Solids	Min. 45%
Ash	Min. 25%
Moisture Content	Max. 50%
Moisture Absorption	Not more than 10%

Both the Steel Structures Painting Council Specification #PS 10.02 64T and AWWA #C-203-62 Section 2.11 refer back to the military specification for the use of coal tar emulsion as a top-coat for exposed steel structures.

6) Fibrated Coal Tar Coatings

These materials are more properly classified as caulking compounds because of their extremely heavy consistencies, but a brief mention of them can be made here. They are basically a mixture of asbestos fibers, mineral fillers and straight coal tar or coal tar pitch and solvent. They find wide application as roofing and flashing cements, as a seal coat between steel tanks and concrete pads, as pipe joint coatings usually with an open mesh fabric, and sometimes on marine piers and pilings where their perpetual stickiness is not a drawback. Many of them will meet the Federal Specification SS-C-153 Type II Coal Tar Base which lists the following requirements:

Federal Specification SS-C-153

Non-Volatile (24 Hrs. at 105-110°C.)	-	70% Min.
Filler by Ignition	-	15 - 45%
Sag at 140°F., 5 Hrs.	-	1/4" Max.
Flexibility at 32°F.	-	No cracking

7) Coal Tar-Epoxy Coatings

Of all the recent developments in coal tar paints, the one which has aroused the most interest has been the epoxy modified composition. As the patent literature shows, almost every resin, polymer or elastomer, has been tried with coal tar in an attempt to make an improved product with varying degrees of success. Some, like the phenolics when mixed with tar and cured, have formed water as a by-product in the coating. Others, like the rubbers, have markedly improved the toughness and elasticity of the system but have added almost impossible restrictions on application characteristics.

The epoxy resins, especially the low molecular weight ones, were found to be miscible in all practical proportions with coal tar and coal tar pitches. No by-products are formed during the cure and viscosity is not seriously affected so that high solids (70 to 100%) coatings can be made. In many respects the addition of epoxy resin eliminates most of the major faults of the coal tar paints. The coal tar epoxy system is semi-thermosetting and thus shows no tendency to run or sag at high temperatures. It hardens but does not become brittle enough to crack or disbond at temperatures as low as 50°F. below zero - it shows no signs of alligating or crazing in sunlight and it retains the low water absorption characteristics

and good adhesion of the coal tar paints. The high solids content of the system permits application of thick films (10 - 15 mils per coat) which harden by chemical reaction rather than by solvent loss. The coal tar-epoxies bleed far less than other coal tar paints and so can be overcoated with color coats or aluminum. The coal tar residual odor problem is minimized and in some instances where special precautions have been taken in the formulation or a heating or baking cure resorted to, the system has been considered suitable for coating potable water tanks and pipelines. In general, however, they are not recommended for use around food or beverage processing plants.

They are resistant to fresh and sea water, fairly strong mineral acids and alkalis, many salt solutions, aliphatic oils, gasoline, kerosene, diesel oils, JP-4 fuel and lubricating oils. In the case of water-white gasoline and fuels, some discoloration may occur and resistance to gum formation should be considered and checked out before using them in this service.

It must be stated here that the improved coating characteristics of the coal tar-epoxies are no cure-all - they have limitations like any other paint system and while, as it has been indicated before, they do eliminate many of the problems common to coal tar paints, they introduce a whole new set of problems of their own. In the first place, the epoxy resin is chemically crosslinked, usually with amines or amides and this introduces a pot-life problem. Most coal tar-epoxies have a usable pot-life of something less than two hours. Another associated problem is that of shelf life - the epoxy and coal tar tend to react to form a copolymer with a viscosity build-up that can be troublesome. In commercial practice, this problem is minimized either by careful selection of the tar or pitch component, or by putting the curing agent into the coal tar and keeping the epoxy resin as a separate component. The general composition of two such products representing the polyamide and the polyamine cured coal tar-epoxies can be illustrated by the requirements extracted from the following published specifications:

A) Polyamide Cured Coal Tar-Epoxy

Steel Structures Painting Council Specification
No. SSPC-PS1164P (July 1964)

(Similar to Paint C-200 - U. S. Army Corps of Engineers)

<u>Ingredient</u>	<u>Component A</u>		
	<u>% by Wt.</u>	<u>Lbs. for</u> <u>3.5 Gal. Batch</u>	<u>Gal.</u>
Coal Tar Pitch (70-75°C. Softening Pt. % Volatile under 250°C.	35.0	13.46	1.28
Liquid Polyamide Resin (97% N.V. Amine Value 330-360)	11.5	4.43	0.55

<u>Ingredients</u>	<u>% by Wt.</u>	<u>Lbs. for 3.5 Gal. Batch</u>	<u>Gal.</u>
Magnesium Silicate	31.0	11.95	0.51
Xylene	18.7	7.20	1.00
Ethyl Alcohol (denatured)	1.0	0.39	.06
Gelling Agent (organic montmorillonite)	1.5	0.57	.04
Catalyst: 2,4,6 (dimethyl- aminomethyl) phenol	1.3	0.50	.06
	<u>100.0</u>	<u>38.50</u>	<u>3.50</u>

Viscosity of Component A - 160 poises Max. (Brookfield)

Component B

Liquid Epoxy Resin (99% N.V. Epoxide Equivalent)	-	9.7	1.0
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B) Amine-Cured Coal Tar-Epoxy

An amine-cured system which has been specified under the Military Specification MIL-P-23236 (Ships) June 1962, Class 2, Coal Tar-Epoxy Coating is described as being composed of a refined coal tar pitch and a minimum of 17% (by weight of coating) of an epoxy resin converted with amines or other suitable materials. It is described as being suitable as a ballast tank coating for fuel (non water-white) and salt water ballast service.

A typical composition for such a system would be as follows:

Component A (20 Parts by Volume)

	<u>Per Cent by Weight</u>
Epoxy Resin, Liquid	30
Selected Coal Tar Pitch	25
Solvent - Coal Tar Hi-Flash	20
Pigment	25

Component B (Curing Agent 1 Part by Volume)

Polyfunctional Aliphatic Amine (Diethylene Triamine or Tetra- ethylene Pentamine)	66.6
Solvent	33.4

The pigment in Component A usually contains a gelling agent to permit the application of heavy vertical films without curtaining or sagging. The two components are mixed just prior to use and applied

by brush, spray or roller to a wet film thickness of 12 to 14 mils (100 square feet/gallon). The dry film thickness then will be 8 to 10 mils. Two coats are generally specified and usually the second coat is applied as soon as possible after the first coat has set to minimize intercoat adhesion problems.

It will be noted that both coating systems are about 80% solids by weight. Some recent specialty coatings used for concrete pipe linings and for non-skid road toppings approach 100% solids by the use of more liquid tars and pitches and epoxy resins. Such systems are very dense, having no solvent pinholes and when loaded with graded aggregate show very little shrinkage on curing, which promotes good adhesion on concrete substrates. More details on the properties and characteristics of one such system will be given in another paper at this Symposium - "A Coal Tar Epoxy Reinforced Concrete Product/System Composite Pipe Structure." One recent innovation has been in the development of a 100% solids pitch-resin combination which is furnished in a powder form. For this material the steel plate or pipe is heated above the melting point of the compound and the powder is applied from a flocking gun, fluidized bed or with an electrostatic gun. The powder melts on hitting the pipe and flows out to form a smooth continuous film. Thickness is controlled by the residence time in the fluidized powder bed and is usually in the range of 10 to 15 mils. Both thermosetting and thermoplastic powders have been tried. Cooling of the thermoplastic coating is accomplished by water spray for quicker handling. In the case of the thermosets, heating often is extended with no water cooling to obtain optimum cure.

The powder is rather costly to manufacture but offers advantages in better physical properties of the coating system. Also where the electrostatic dusting method is employed, there is practically no overspray loss and odd shapes can be coated with ease.

This system is still in its infancy but looks extremely promising for many special applications.

Future Trends

It is believed that future improvements and modifications of the cold applied coal tar coatings will probably follow the trends of the recent past. Low molecular weight coal tar pitch definitely requires an assist from the high molecular weight resins and polymers to increase its toughness, flexibility, and temperature sensitivity while retaining the already well established special properties of low cost, low water absorption, high microbial resistance and long-time service performance.

COLD-APPLIED ASPHALT COATINGS

by

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In the field of protective coatings today, the consumer has an extremely wide and constantly growing choice of excellent materials to cope with almost any need. Among them there is an engineering material whose known history of useful application probably surpasses that of any of the others. In the world of coatings it is indeed a "Plain Jane". It is not available in two dozen assorted colors, but like Henry Ford's Model T, it comes in just one, -black, - though it is capable of limited pigmentation.

It may be described as an almost entirely utilitarian material, very seldom decorative, and yet it is being used at present at a rate estimated at 25 million tons annually. This material is asphalt. With such a rate of usage, there must be much that can be said for it. There is. It is highly water resistant, has excellent adhesive properties, it can be quite resilient and ductile, it is durable in many applications without any modifications, and can be compounded to further increase this property; it has a versatility matched by few, if any, similar engineering materials, and it offers all of the above properties, plus numerous others, at a low cost that makes it quite a bargain in today's burgeoning coatings market.

It is known that asphaltic bitumens were used as far back as 8000 years ago. An actual specimen of asphaltic foundation coating is still in existence today in Iraq - four thousand years after it was applied. I've often wondered what the original contractor's guarantee was for this job.

SOURCES-

All of these early asphalts were simply seepages of more or less viscous materials. The natural or "mined" asphalts today such as the famous Trinidad deposits, gilsonite, etc. constitute a small but useful segment of the industry, but the vast bulk of today's asphalts are of petroleum origin. They are in plentiful supply, of high and consistent quality, and capable of being "tailored" to a wide variety of uses. They are in no sense "man-made" asphalts, for they are present as such in the original crude petroleum, and the process of separating them is purely physical, usually by distillation, either atmospheric or vacuum. Those ancient seepages, as well as today's mined asphalts, are also products of a distillation process, but one which nature, never in a hurry as man always seems to be, has taken centuries to complete.

Once this separation has been effected, there are many ways in which the product can be modified. Probably the most used, as well as most useful modification is air blowing, usually referred to - incorrectly - as oxidation. By blowing finely divided air through the asphalt at elevated temperatures, both physical and rheological changes are made to occur. Broadly, these may be considered to be the result of dehydrogenation and condensation of unsaturated linkages. The air blowing process has been expanded by use of "catalysts", which further improve the temperature susceptibility, penetration index, ductility, and other desirable characteristics.

Asphalts are thermoplastic materials, and may therefore be applied in the molten state. Though somewhat cumbersome, this method does have the advantage that the application is fully ready for its intended use as soon as it has cooled. But for many uses, especially those that may be called "field" uses, there is a distinct need for asphaltic coatings that may be applied cold, without the need for special equipment, or the element of haste (because of cooling) or danger inherent in handling molten asphalts.

COLD-APPLIED COATINGS

It is with these cold-applied asphaltic coatings that we will be concerned at present. These products should not be considered only as a convenient way of applying a coating that would otherwise have to be melted, for they often can be formulated to do a job completely impractical or even impossible with a hot-melt coating.

The two methods for modifying asphalt so that it may be applied cold are similar to those used by the paint industry to apply various resinous coatings. They may be dissolved in a solvent, or made into an aqueous emulsion. A long line of useful products is produced by both methods, with each type having its own distinct characteristics and uses.

THE CUTBACKS

Solvent-base coatings, or "cutbacks", so-called because they are cut back or diluted with solvent, are made by the simple expedient of dissolving the asphalt base in a compatible solvent, usually of petroleum origin, until a usable consistency is obtained. The resulting solution, when applied as a coating, dries as a lacquer, by loss of solvent alone. Drying rate may be controlled over a wide range by selection of solvents of varying evaporation rates. Two considerations that must always be borne in mind is that the diluting medium must have adequate solvent power, and that its flash point must stay at a safe level. In the case of the former, poor viscosity stability and poor film integrity can result from an ill-chosen solvent system. As for the latter, the inherent flammability of any solvent base coating must be kept in mind at all times, both from the point of view of safety and of shipping regulations. It must be remembered that the same volatility that speeds drying also lowers the flash point. In special instances cutbacks can be made non-flammable in the wet state, usually by use of chlorinated solvents, but these can have their own problems. They are considerably more expensive, and must be chosen with great care due to the potential toxicity involved.

Because of their low surface tension, asphalt cutbacks have excellent wetting and penetrating power, and for this reason are often used as primers for hot-applied asphalts as well as for the filled mastics of the types that will be described later. Without fillers or modifiers, cutbacks have limited use where exposed to the ravages of weather. Some of the earliest modifiers were various resins and drying oils, of which literally hundreds have been used, to produce an assortment of bituminous lacquers and varnishes.

If it is desirable to obtain greater "build" of a coating, whether this be for greater weatherability, better vapor barrier characteristics, higher strength, improved abrasion resistance or for other reasons, the use of mineral fillers becomes highly important. The properties generally sought in the filled coatings are:

- (1) Resistance to flow or deformation under any temperature or climatic condition likely to be encountered.
- (2) Resistance to mechanical abrasion and attrition, while maintaining strong adhesion to the substrate.
- (3) Strong cohesive properties, affording internal strength.
- (4) Maximum weather resistance, a property often associated with a choice of fillers having maximum opacity to actinic rays.

Not all fillers can fill the above requirements. Fillers that are excessively hygroscopic, have too high oil absorption, that are vulnerable to chemical vapors, or that are transparent to actinic rays can cause early failure of a coating. This last property is quite important since all asphalts are subject to photo-oxidation. This is largely why asphalt shingle roofs are so durable, with the opaque roofing granules throwing up a protective shield, as it were, for the asphalt coating beneath. A novel method, in fact, for adding to the durability of an asphalt cutback coating, has been the spraying of roofing granules onto the still wet mastic, so that they are permanently imbedded when the coating has dried.

Asbestos fibers are one of the many widely used fillers. Others are slate flour, rock dust, limestone, clays, ground slag, diatomaceous earth, silica, cork, vermiculite, mica, cotton and wool fibers, along with countless others. A happy aspect of the use of fillers is that while they can greatly improve the product, they often lower the cost, since they are usually less costly than the asphalt and solvent that they displace. If maximum vapor barrier characteristics are desired, a minimum of hygroscopic fillers and fibers must be used.

APPLICATIONS

The largest single use for asphalt cutbacks is in the construction of pavements, but this is a separate field in itself, not intended for the scope of this discussion. Another high-volume use is in the waterproofing and damp-

proofing of structures, the difference in the terminologies referring simply to whether the coating is applied below or above ground level. Below ground, where temperature changes are comparatively small, and there is no exposure to light and air, the properly designed asphalt coating has few peers. It can normally be expected to outlive the structure it is designed to protect. Where used above ground for dampproofing, the coating is intended to prevent the inroads of dampness and moisture on masonry surfaces.

Heavily filled asphalts of brush, spray and trowel grades are used as industrial coatings and give many years of service. A weathered surface can be resurfaced readily with a cutback-type coating, which will form an excellent bond to the old coating. It was said earlier that asphalt is seldom decorative. One of the few exceptions is asphalt aluminum paint, in which a leafing grade of aluminum powder is added to an asphalt cutback of high fluidity. When it is applied as a paint, the aluminum leafs or floats to the surface to form a metallic coating that is not only attractive but which increases the life of the coating several fold. By use of higher percentages of aluminum, heavy aluminized mastic coatings can be made that have exceptional resistance to weathering, and show high reflectance and consequent insulating value. A relatively recent innovation has been the introduction of asphaltic coatings incorporating high loadings of non-leafing aluminum along with colored pigments, to produce bright metallic pastel coatings of exceptional durability, that show no visual evidence of their humble parentage. These attractive colors may well be asphalt's finest hour, esthetically speaking.

Another limited, but less spectacular variation from asphalt's black color has been the incorporation of certain red oxide pigments to produce various shades of red and brown. For the best results, an asphalt should be selected that has a brown, rather than a black cast when examined in thin films by transmitted light.

Sound deadening coatings make use of the visco-elastic properties of asphalt. These materials find volume use not only in the automotive industry, but for metal cabinets, office furniture, bathtubs, air conditioning equipment, household metal furniture and panels where vibration and drumming must be damped. Underbody protective coatings for cars and railroad rolling stocks use not only the waterproofing and adhesive properties of asphalt, but its ability to withstand abrasion and impact as well.

All of us are familiar with the annoyance of "sweating" of cold surfaces in a damp location. A well-proven cure for this malady, which can be expensive as well as annoying, is the application of an asphalt mastic filled with either ground cork or vermiculite, or both. We are thus given insulating value plus waterproofing in a single material.

Looking further into the subject of insulation, it is well known in the industry that a good vapor barrier is essential over low temperature insulation. Without it, condensation, and even ice formation, can seriously reduce the thermal efficiency of an insulation, and even destroy its mechanical integrity. In this respect, solvent based asphalt coatings, even those with moderate filler loadings other than those described in the previous paragraph, have very low moisture vapor permeability, and are well known and regarded where this requirement is paramount. This topic will be expanded later.

We have referred several times to the adhesion characteristics of asphalts, so it is only to be expected that we will see them find their way into

uses where this property will be put to use. It finds many uses in hot-melt adhesives, emulsion adhesives, and also in the one being discussed at the moment, the solvent based asphalt field. Typical examples of the latter are the asphalt floor tile adhesives used so extensively today. Completely unaffected by dampness or even flooding, they are as durable as the flooring itself. It is a safe assumption that the floor tiles in the offices of most of those here present are adhered with asphalt.

If coatings of the types discussed above are to protect against the inroads of water, it seems reasonable that any surface water must be removed before the coating can be properly applied. Sometimes it is impractical to produce a bone-dry substrate, so a simple way of circumventing the problem is the incorporating of various water-displacing compounds, such as oil-soluble sulfonates, phosphates, amides, amines, metallic soaps, fatty acids, etc. These same additives can act as rust inhibitors when the coating is applied over metal.

Asphalt coatings have been outstandingly successful in protecting numerous concrete and wood structures against the destructive action of mineral acids, acid salts, alkalis, and many corrosive chemicals. Concrete, especially, requires such protection, since Portland Cement is very susceptible to acid of any strength. Another large volume usage of filled asphalt mastic coatings is in protection of metal surfaces of tanks and various structures from corrosive industrial environments. The mastics are available in various grades, with choice depending on method of application and film thickness desired. Primers often are recommended as added protection against penetration of corrosion beneath the edges or at locations of unavoidable voids in the coating. Asphalt primers or several synthetic base primers are compatible with most asphalt coatings.

Asphalt is, of course, a flammable hydrocarbon, and coatings deposited by any method will burn. They are difficult to kindle, however, having flash points generally in the order of 500 - 600°F. The incorporation of fillers appreciably decreases this flammability. To carry this further, we can formulate coatings that are made highly fire retardant by several methods, such as blending with various chlorinated resins, usually in combination with antimony trioxide. It is also possible, as pointed out earlier, to incorporate a non-flammable solvent system in the composition.

In addition to the virtues listed above for cutback asphaltic coatings, another very significant attribute is their adaptability to application in very thick coatings. Where a conventional paint may be reckoned in terms of 2 or 3 mils per coat, it is not uncommon for an asphaltic coating to be applied at a rate 30 or 40 times this amount. This obviously greatly increases the protective qualities of the coatings, while expanding their utility.

ASPHALT EMULSIONS

The other category of cold-applied asphalt coatings is that of the aqueous emulsions. Here we have the same basic situation as that existing with

any other emulsion: two immiscible liquids, one dispersed into the other as very minute particles, and prevented from coalescing and returning to a separate continuous phase by the presence of an emulsifying agent, sometimes referred to as a stabilizing agent, suspending agent, dispersing agent, etc. Asphalt emulsions may be divided into two broad categories, the chemical or soap emulsions, and the clay emulsions. The former group may in turn be divided into anionic, cationic and nonionic emulsions.

The chemical emulsions are made possible by the presence of an emulsifying agent that must be compatible with both the water and asphalt phases. A graphic visualization of such an emulsion would depict a discrete droplet of asphalt, probably about 4 microns in size, completely surrounded by the external phase, water. The molecules of the dissociated emulsifier would appear as a continuous layer around the asphalt particle, and would be so oriented that their non-polar or organic portions would face towards the asphalt particle, while their polar portions would orient themselves outward towards the water phase. This heads-and-tails arrangement affords a basis for understanding much about both the manufacture and performance of emulsions. It has been calculated that a 65% solids emulsion of the above particle size contains approximately twenty billion asphalt particles per cubic centimeter, each entirely separate, and held at arm's length from its neighbors, as it were, by the interfacial molecular forces as described above.

If the organic portion of the emulsifier, which governs its property as an emulsifying agent, contains a negative charge, it is called anionic. The particles of asphalt will acquire a negative charge, and will be attracted towards a positively charged surface. Exactly the reverse is true in a cationic emulsion in which the positively charged asphalt particles are attracted towards a negatively charged surface. A non-dissociating emulsifier imparts no particular charge to the asphalt particles, thus forming a nonionic emulsion. The above classifications have significance when we are concerned with obtaining optimum wetting and coating of various substrates. These properties are of great importance in the wetting of fillers and aggregates, whether this be in the manufacturing stage or in job-site applications. It is of particular concern where emulsion-type pavements are being laid.

In an asphalt clay emulsion, the same equilibrium of forces between the two immiscible liquids must be maintained, but in this instance a mineral clay acts as the primary emulsifying and stabilizing agent. In general, clay minerals which are wet readily in water, and which will disperse as colloidal particles, will act as effective emulsifiers for asphalt in water. A number of clays are able to do this, such as kaolinite and attapulgite, but there is one clay, bentonite, which stands alone in its efficiency as an emulsifier. It is a montmorillonite clay of unique crystalline configuration, which is as much as ten times as efficient as other clay emulsifiers.

COMPARISON WITH CUTBACKS

All asphalt emulsions are made by high-shear dispersion of the asphalt in the water phase, in which the emulsifier is already present. This usually

has to be at a temperature high enough to fluidize the asphalt, but not so high as to cause the water to boil. These emulsions are quite a breed apart from the solvent or cutback-type coatings previously discussed. They obviously involve no fire hazard for the applicator, being water-based. The usual rules of volatility do not apply, as water is the only volatile present. In general, they will dry faster than a solvent-applied coating of comparable thickness, since the water has no affinity or solvent effect on the asphalt, as is the case with cutbacks. Whereas cutbacks usually tend to dry from the top down, thereby forming a skin that will slow the drying rate, clay emulsions tend to dry from the bottom up, and will dry to full hardness faster. Chemical types may skin, but still will dry rapidly.

The solvent in a cutback coating gives maximum fusing of the asphalt into a dense mass on drying, whereas the disperse nature of the asphalt particles in an emulsion generally produces a coating more permeable to water vapor. Most "breather" coatings are emulsions, though incorporation of certain porous fillers can make a normally tight vapor barrier cutback coating into one that would be classed as a "breather". The terms vapor barrier and breather are relative, and somewhat arbitrary, but as a rule of thumb a breather should have a minimum perm rating of approximately 1, while the vapor barrier should have a rating of 0.5 perm or less, with very low temperature applications having an allowable maximum of 0.1 perm. Both coatings have specific areas of use. The vapor barrier is designed to block the ingress of water vapor due to the vapor pressure differential that exists on the opposing sides of a coating, such as on an insulated storage tank, which is operated at a temperature below ambient. The breather is designed to allow the escape, as a vapor, of any moisture trapped between a coating and a surface maintained at a temperature above ambient. The penalty for choosing the wrong coating can be severe in either instance. An inadequate vapor barrier, for example, will allow insulation to become water-logged and less efficient, and if the temperature is low enough, heavy ice buildup can result below and inside the insulation. A coating that won't breathe when it should, on the other hand, is almost sure to blister, lose adhesion and have its useful life shortened. A property common to both coatings is that both are equally impervious to liquid water, and must be able to withstand the ravages of weather.

APPLICATIONS

Many of the uses of emulsions parallel those of the cutbacks. They accept fillers readily, but more care must be taken in their choice for a given type of emulsion. They have good adhesion to clean surfaces, and the chemical types have wetting characteristics that can approach those of the cutbacks over dry surfaces, and readily surpass them over damp surfaces. Emulsions are used as foundation coatings, sound deadeners, underbody coatings, roof coatings, insulation coatings, masonry coatings, concrete curing agents which prevent excessive surface evaporation as the concrete cures, and they combine with Portland Cement to produce flooring compositions that exhibit many desirable features of both asphalt and concrete. The list is long. The clay emulsions have a thixotropic body which facilitates thick applications on surfaces other than horizontal, and their dried films have a static quality that will not allow them to flow even on direct exposure to flame. The bentonite clay forms a net-

work structure in the coating which gives it outstanding durability. There are coatings of this type which are in excellent condition after over 35 years of outdoor exposure, and which may well endure for another 35 years. Strangely, bentonite will not impart this exceptional durability to asphalt when it is incorporated by any other method. Asphalt emulsions are today a staple item in many fields, with total sales of approximately 600 million gallons annually.

A special class of asphalt protective coating is that of roofing. This may differ from other coating applications for several reasons. For one, the pitch of the roof may vary over a wide range, all the way to dead level, on which there will often be layers of water in contact with the coating for prolonged periods. Another is the reversed vapor pressure differential which can exist on a roof in cold weather, causing water vapor to try to get out rather than in.

We have all seen hot-applied built-up roofs under construction, with the smoking melting kettle, and the mopping of the several plies of felt in overlapping layers. The same type of built-up roof can be constructed using only cold-applied coatings such as described above. In general, it is preferred that the two or three plies of saturated felt be laminated with cutbacks rather than emulsions because of their better drying and cementing characteristics under these conditions. The top, or weather coat may be of either the cutback or emulsion type, with preference towards clay emulsions where maximum life is desired. Ten and fifteen year bonded roofs by this process are common, with the bonds being extended to twenty years when the roof is surfaced with ground slag or gravel.

It should be noted that almost no other construction material today is covered by such a generous bond. It should also be mentioned that a properly applied built-up asphalt roof may well give double the service life of the bond.

A newcomer in the roofing field, but one which has exceptional promise, is one in which a special gun is used to spray clay emulsion and chopped glass fiber simultaneously through separate nozzles, to lay down a thick glass fiber reinforced monolithic roof in a single application.

A field that has been penetrated moderately by the cold-applied asphalts is that of underground pipe coatings, which are designed to protect the tens of thousands of miles of large-diameter pipelines that transfer natural gas, petroleum and other products for great distances. The hot applied coatings still comprise the bulk of present usage, with special machines applying the hot coating and wrappings for mile after mile along the main line. But for field coating of gathering lines, valves and fittings, application of cold-applied asphalt forms a useful complement to the system. Cutback mastics are usually used for this purpose.

Both the cutbacks and the emulsions can be applied by the conventional methods of the trade, such as spray, brush, trowel, roller, etc. requiring no specialized equipment or training on the part of the applicator. Each type has its uses, each type has its precautions.

While the cutbacks are flammable, the emulsions can freeze. The emulsion dries faster than the cutback, but is more vulnerable to unexpected rainfall, and so on. Most of these are routine considerations well known to anyone in the protective coatings trade, and not unique with asphalt. The dried coatings may be dissolved by petroleum or other type solvents, but this rarely presents a problem in actual conditions of use.

This has often been called The Space Age, and it has become a symbol of prestige for an industry or a product to become associated with it. The highest distinction comes when a product or a material becomes incorporated as part of some space age flying hardware. I am happy to report that asphalt has made the ranks of this industrial elite. We have learned recently that an asphaltic deadener pad assembly has been specified for vibration damping of certain electronic components of one of our missiles. This use, however, totals only a few ounces of asphalt per missile, so it is apparent that asphalt's future will remain earthbound, instead of in outer space. But this should be no hardship, since both past and present experience indicate that as long as Mother Nature continues to furnish this versatile material, man will find abundant uses for it.

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TABLE I

UNFILLED ASPHALT COATINGS

ASPHALT PRIMER

Asphalt (20 -70 penetration)	35 - 55%
Solvent	45 - 65%

COLD DIP PIPE COATING

Asphalt (10-30 penetration)	30 - 50%
Solvent	50 - 70%

ASPHALT ALUMINUM PAINT

Asphalt (10 -30 penetration)	25 - 35%
Solvent	40 - 60%
Aluminum powder	15 - 25%

Consistency: 100 - 2000 cps.

Coating Thickness: 2 - 8 mils.

TABLE II

SPRAY AND TROWEL GRADE WEATHER RESISTANT COATINGS

CUTBACK MASTIC, SPRAY GRADE

Asphalt (30 - 50 penetration)	30 - 50%
Asphalt fiber (and fillers, if used)	10 - 20%
Solvent	30 - 60%

Consistency approx. 10,000 - 40,000 cps.

Coating Thickness: 1/32" - 1/8"

CUTBACK MASTIC, TROWEL GRADE

Asphalt (30 - 50 penetration)	40 - 55%
Asbestos fiber (and filler, if used)	15 - 30%
Solvent	15 - 45%

Consistency approx. 50,000 - 100,000⁺ cps.

Coating Thickness: 1/16" - 3/16"

TABLE III

VARIOUS CUTBACK MASTIC COATINGS

CUTBACK-BASE AUTOMOTIVE AND RAILROAD CAR PROTECTIVE COATING

Asphalt (15 - 30 penetration)	30 - 50%
Asbestos fiber (and filler, if used)	20 - 30%
Solvent	30 - 40%

Consistency: Spray
Coating Thickness: 1/16" - 1/8"

CUTBACK-BASE SOUND DEADENER

Asphalt (40 - 60 penetration)	15 - 25%
Asbestos fiber	5 - 10%
Fillers	40 - 50%
Solvent	15 - 30%

Consistency: Spray
Coating Thickness: 1/16" - 1/8" (approx. 1/2 lb./ft.²)

CUTBACK-BASE ANTI-SWEAT COATING

Asphalt (10 -20 penetration)	30 - 40%
Asbestos fiber	8 - 15%
Lightweight Filler (cork, vermiculite, etc.)	4 - 8%
Solvent	35 - 50%

Consistency: Spray
Coating Thickness: 1/8" - 1/4"

TABLE IV
TYPICAL ASPHALT EMULSIONS

ANIONIC SOAP EMULSION

Asphalt (40 - 200 penetration)	58 - 70%
Emulsifier (e.g.: vinsol or rosin)	1 - 3%
Water	30 - 40%
Viscosity range: 100 - 20,000 cps.	

CLAY EMULSION

Asphalt (100 - 200 penetration)	50 - 60%
Bentonite clay	1.5- 3.0%
Water	40 - 50%
Viscosity: 6,000 - 20,000 cps.	

TABLE V

WATER VAPOR PERMEABILITIES (WET CUP METHOD)

<u>Product</u>	<u>Typical Usage Dry Film Thickness, Inches</u>	<u>Perms at 77°-55°F</u>
Oxidized Asphalt	1/8"	0.01 - 0.02
Mineral filled Asphalt Cutbacks	3/32"	0.02 - 0.04
Cork filled Asphalt Cutbacks	3/16"	0.04 - 0.09
Asphalt Clay Emulsion	3/32"	0.2 - 0.6
Polyethylene Film	0.004	0.16
Plasticized Vinyl Chloride	0.02	0.29
Polystyrene	0.005	0.7
Waterproof Cellulose Film	0.002	58

TABLE VI

GENERAL PROPERTIES OF ASPHALT COATINGS

Application	Asphalt Cutback Coatings	Asphalt Cutback Mastics	Clay Emulsion Coatings
Spray	Yes	Yes	Yes
Brush	Yes	Limited	Yes
Trowel	No	Yes	Yes
Temperature Range, °F	50-110	50-110	40-110 (Lower if winterized)

Fire Resistive Properties

Wet State	Flammable, unless special solvents used.	Flammable, unless special solvents used.	Non-flammable.
Dry coating	Flammable	Static under flame, supports combustion to limited extent.	Static under flame, supports combustion to limited extent.

Properties of Dry Coating

Oil & Grease Resistance	Poor	Poor	Poor
Resistance to Mild Acids	Excellent	Excellent	Excellent
Resistance to Mild Alkalis	Excellent	Excellent	Excellent
Abrasion Resistance	Poor	Good to excel.	Good
Outdoor Weathering	Fair	Excellent	Excellent
Flow at 300°F	Poor	Good to excel.	Excellent

A COAL TAR-EPOXY REINFORCED CONCRETE PRODUCT/SYSTEM
COMPOSITE PIPE STRUCTURE

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ABSTRACT

Extensive uses of coal tar-epoxies in protection of steel have been documented and reported in the technical literature. New and important uses of this resin system in protection of other materials of construction are reported. This paper presents a coal tar-epoxy product/system for protection of concrete sewer pipe lines subjected to corrosive attack. The materials engineering system consisting of coal tar-epoxy resin with reinforced concrete, and the unique method of manufacturing resulting in a composite pipe structure, are discussed. Mechanics of corrosion of concrete sewers and remedial measures are explained. Laboratory, environmental, and field chemical resistance studies, as well as physical properties, and beneficial effects of the coal tar-epoxy product/system on the structural behavior and design of circular reinforced concrete pipes, are presented.

SOME LABORATORY EVALUATIONS OF BITUMINOUS COATINGS

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Bituminous Substances have been used as preservatives and protective coatings for thousands of years. Their effectiveness is based largely upon their resistance to moisture and chemical attack. The term "Bituminous Substances" includes a wide variety of chemical compounds. These are the native asphalts, oils and resins, of both animal and vegetable origin, the products derived from them by further treatment and chemical means, the refined and chemically treated petroleum asphalts and coal tar products, and the pitches and residues from the treatment and processing of resins and oils.

The current major volume of bituminous materials, by-products of the coal and petroleum industries, have been developed and used as protective coatings over a long period. This has been due to their ready availability, low cost per unit volume and to their performance characteristics.

Many bituminous compounds have performed as underground protective coatings exposed to soil and water for a half century. With such long service performance, shorter-term laboratory performance tests are a requisite in order to evaluate the newer bituminous compounds, other coatings, and particularly those applied at lesser film thicknesses than in past practices.

In corrosion control the most effective property of a coating is electrical insulation. The proper insulative values limit galvanic and cell type corrosion. This fact applies generally, for coatings used both above and below ground or

immersed in electrolyte. Water may destroy mechanically, by water sorption and desorption, coatings in transient water exposures, flexing the coatings to physical failure. Water may destroy the electrical insulation property of coatings by penetrating and carrying in electrolytes and acting as an ionizing vehicle to solubilize coating constituents. Water-saturated coatings are, in effect, a broth of electrolyte and have very limited protective values for metal. Therefore, to preserve the utmost coating integrity and performance, water must be excluded.

In order to accomplish this, the compounder must produce a coating which will resist water absorption at least to a degree sufficient to prevent its being penetrated by water to become water-saturated and thereby electrically conductive. The compounder must develop means of evaluating the materials already known to have excellent performance in this property and means of studying these materials in relation to new compounds and systems.

The criteria which must be determined in order to produce new coatings equal to past excellent ones are: (1) water absorption; (2) water penetration; (3) water saturation; (4) electrical insulation values; and (5) performance in relation to the flow of galvanic currents.

WATER ABSORPTION

Much work has been done in determining the water absorption properties of coal tar and asphalt by gravimetric methods^{1, 2}. Earlier workers applied coatings to glass or metal and determined the sample weight increases after immersing in

water for various periods of time³. The increase in sample weight generally was expressed as an increase percent by weight and was assumed to be entirely due to the absorption of water. In most cases the possibility of solution of the sample or sample loss to the water was not considered. A.S.T.M. Method D-95 uses flat free films of the coating material as samples and in this method the actual water absorbed is removed from the weighed sample, collected and measured⁴. The results may be expressed either as weight percent increase, or as weight per unit area exposed to the water. Most workers agree that for coatings which may vary widely in specific gravity, it is preferable to express the figure as weight gain per unit of area exposed.

The samples of this paper were prepared as free films by coating on Mylar sheet and stripping after cooling or drying. Either hot- or cold-applied materials may be stripped from Mylar. The removal of most tacky compounds can be effected by chilling the sample. The free films are cut to measure approximately 5.0 x 10.0 cm. per side. The thickness is approximately 100 mils. The exposed area is calculated to be roughly 100 sq. cm. These samples are (after sponging dry the surfaces) immersed in tap water of 70,000 ohms cm³ resistivity and are weighed at intervals for a period of 1,000 hours. This period was chosen after it was discovered that no trend of early equilibrium could be established in short-term gravimetric tests. This is also evidenced by the work of Henry Lee⁵. In most cases, after attaining the gravimetric-time curve for at least 1,000 hours, the samples are removed and a desorption or weight loss-time curve is obtained. It was found that such a procedure depicts any loss in weight

by leaching from the sample.

Figure 1 shows gravimetric curves for hot-applied plasticized coal tar enamel and for room-temperature cured coal tar-epoxy. The exposure was at 70°F and demonstrated that at this temperature there is some leaching loss with the plasticized coal tar enamel and none with the epoxy compound. The leaching effect can be so pronounced as to become the major effect with some bituminous substances such as Gilsonite (Figure 2) which continuously dissolves in water at room temperature.

A number of gravimetric absorption tests were made at 160°F, and it was found that practically no bituminous material, either coal tar or asphalt, was suitable for exposures at these temperatures. As shown in Figure 3, coal tar enamel at 160°F absorbs more than twice as much water as it does at 70°F. The leaching effect in this example is not noticeable at 70°F. It is, however, considerably more pronounced than the absorption effect when carried out at 160°F. For a total of thirty bituminous samples tested at 70°F and 160°F, the average absorption at 160°F was approximately fifteen times that at 70°F. A series of bituminous materials representing those which are most resistant to water absorption is shown in Figure 4. From this chart, one may determine that both asphalts and coal tar materials can be highly resistant to water absorption at room temperature. It is also shown that certain solvent solution cold-applied materials are as resistant as the hot-applied resins. The asphalts, other than asphalt enamel, are all blown asphalts of similar physical properties but of different origin. They vary more in absorption properties at 160°F than at 70°F. It would appear characteristic

of coal tar types to leach somewhat at 70°F and considerably at 160°F. With asphalt types this is not evidenced.

Aside from the inherent water susceptibility of a particular bituminous resin itself, it is characteristic that the presence of loading compounds, fillers, talcs, etc., in such a bituminous coating compound can seriously affect the properties of water resistance. While pigments and loading compounds are frequently added to improve the physical properties of tensile strength, flow and deformation resistance, hardness, etc., pigmentation always results in increased water absorption. It is essential, therefore, that only pigments low in water susceptibility and ion content be used, in order to keep water absorption low and to prevent water saturation and electrical conductivity upon prolonged exposures to water.

Figure 5 demonstrates the effect of variations in weight percent additions of such a carefully chosen pigment to a cold-applied insulative asphalt coating. The exposure was at 70°F. While 25% additions do not markedly increase water absorption above the value for the resin alone (30 milligrams) percentages higher than this are certainly clearly detrimental to water absorption resistance. Typical values for coal tar and asphalt enamels are found to be in the range of 20 to 35%.

It should be pointed out that the degree of water absorption in coating materials is determined to a large extent by the effects of osmotic pressure. Elm⁶ showed that the higher the osmotic pressure of a solution the lower the rate of water absorption. Using distilled water, he found no equilibrium

established after 800 hours of immersion. Elm also pointed out the increased water absorption in films subjected to potential gradients, the electroendosmotic effect. It can be understood, therefore, that solution gradients produced by chemical electrolytes are quite apt to be different than those produced by distilled or tap water. For this reason, as well as due to specific chemical reactivities, electrolyte weight absorptions may vary from those obtained with water with the specific electrolyte and with the particular bitumen or coating compound. (Figure 6).

WATER PENETRATION BY ELECTRICAL METHODS

A number of workers have explored methods to relate electrical measurements to water absorption and to water saturation of coating materials. Arthur⁷ points out the value of electrical resistance measurements as a means of determining "failure to protect." His test is not an accelerated test.

While the volume resistivity values of most bituminous substances fall in the range of 1×10^{12} ohms cm.³ to 1×10^{15} ohms cm.³, there occurs a wide variation in their resistance values measured during immersion in water. From time to time, resistance values may vary up or down 10, 100 or even 1,000 times the prior reading. Adventitious pinholes or conductive leakage paths are formed giving little indication as to whether the entire coating volume is conductive or merely a single tiny area.

Conway and Smith⁸ suggest the use of magnetic resonance to determine the moisture content in hygroscopic materials. While

the method is non-destructive and fast, it may not prove suitable for use at low percentage values of water in coatings such as are found with bituminous materials. McKinley and Seaberg⁹ used gravimetric data, specific inductive measurements, and power factor values to set up minimum specification performance criteria for cable insulation. They showed early failures with voltage and current stresses, but they could not demonstrate a suitable short-term test to predict insulation breakdown.

Brasher and Kingsbury¹⁰ in 1954 set forth a comparison of gravimetric methods and capacitance methods for measuring water absorption. They pointed out that it is possible to estimate water up-take from the capacitance changes that occur during the immersion of the painted panel. They suggested methods of water distribution within the coating and that possibly water is distributed in layers parallel to the coating surface.

At the time of such early workers, we developed a method particularly suitable for the water-capacitance evaluation of bituminous compounds. We found that the distribution of water in these insulative type coatings with limited concentrations of pigments could be considered to be essentially in layers parallel to the sample surfaces. For most bituminous type coatings we have been able to corroborate this, and we have also found it particularly valuable to relate the changes in capacitance to a calculated value of the actual depth of penetration of the water front into the sample.

Whereas, volume resistivity values indicate either pinhole penetration or absorption or a combination of both in a

qualitative fashion, the dielectric constant values more nearly indicate the water absorption, quantitatively. While an adventitious pinhole may affect the volume resistivity reading adversely, and change the value by its presence several thousand percent, it will produce only a small effect in the dielectric constant value of the sample.

Since the dielectric constant value of immersion water is from eighty to several hundred times that of air and since the dielectric constant values of electrically insulative bituminous coatings are much nearer to those of air than to the values of water or electrolytes, the inclusion of water within an insulating coating material so markedly changes its dielectric constant value that a sensitive index to quantitative absorption and depth of penetration is provided.

A series of dielectric constant values readily obtained from water immersed samples furnish indices to the quantity of water absorption or depth of penetration of water saturation at any instant. When these values are taken over a period of time and the capacitance values indicate that the value of dielectric constant for the sample is 81 (distilled water), water saturation and penetration are complete and the coating will have little, if any, protective value.

The rate of water absorption with time may be plotted and the theoretical t_1 , or penetration depth, may be used as an index of coating performance.

After only a few weeks exposure, curves of t_1 values versus time show a tendency with good coating material to establish t_1 at a very low rate of change. Study of these

early curves furnishes an index of ultimate performance and aids in establishing a predicted time of saturation failure.

A condenser specimen is set up using a 4" x 10" panel on which is placed a uniform coating. The thickness is measured accurately. A one pint can with bottom removed is placed against the dried coating and sealed around the edge with caulking compound. The can is then filled with water, thus forming a parallel circular plate condenser with water as one plate and the steel panel as the other (Figure 7). The diameter of the can is measured to calculate the area of one of the plates.

Immediately, upon filling, the initial capacitance and resistance are measured. The specific inductive capacity (K_0) for the whole coating insulation is calculated by using the following equations for parallel circular plate capacitors:

$$C_0 = \frac{.0885 K_0 \cdot S}{t} \qquad K_0 = \frac{C_0 t}{.0885 \cdot S}$$

Where in the above; (initial capacitance reading) C_0 is in micro micro farads (MMfd.), K_0 is the dielectric constant, S is the area of one plate in square centimeters, and t is the thickness in centimeters.

By considering the coating as made up of two series circular plate capacitors (Figure 8) composed of (1) C_1 a thin capacitor of water-saturated dielectric insulation, and (2) C_2 a thicker capacitor of water-free dielectric insulation, calculation of the approximate water penetration depth, t_1 , can be made.

$$\text{The total capacitance } C = \frac{C_1 \cdot C_2}{C_2 + C_1}$$

The capacitance for the water-saturated dielectric insulation layer is: $C_1 = \frac{.0885 \cdot 81 \cdot S}{t_1}$ Note: $K_1 = 81$

The capacitance for the water-free dielectric insulation layer is: $C_2 = \frac{.0885 \cdot K_2 \cdot S}{t_2}$ $K_2 =$ the initial K_0 value calculated

Equations:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2}$$

$$\frac{1}{C} = \frac{1}{\frac{.0885 \cdot 81 \cdot S}{t_1}} + \frac{1}{\frac{.0885 \cdot K_2 \cdot S}{t_2}}$$

$$\frac{1}{C} = \frac{t_1}{.0885 \cdot 81 \cdot S} + \frac{t_2}{.0885 \cdot K_2 \cdot S}$$

Also:

$$t = t_1 + t_2$$

$$t_2 = t - t_1$$

$$\frac{1}{C} = \frac{t_1}{.0885 \cdot 81 \cdot S} + \frac{t - t_1}{.0885 \cdot K_2 \cdot S}$$

$$\frac{1}{C} = \frac{t_1}{7.1685 S} + \frac{t - t_1}{.0885 \cdot K_2 S}$$

The value for K_2 is the same as for K_0 at the start of the test when $t_1 = 0$ i. e.

$$C_0 = \frac{.0885 \cdot K_2 \cdot S}{t} \quad \text{and} \quad K_2 = \frac{C_0 t}{.0885 \cdot S}$$

Then, substituting for K_2 :

$$\frac{1}{C} = \frac{t_1}{7.1685 \cdot S} + \frac{t - t_1}{\frac{C_0}{.0885} \cdot S} \quad (.0885 \cdot S)$$

$$\frac{1}{C} = \frac{t_1}{7.1685 \cdot S} + \frac{t - t_1}{C_0 \cdot t}$$

$$7.1685 C_0 \cdot S \cdot t + C \cdot C_0 \cdot t \cdot t_1 + 7.1685 C \cdot S (t - t_1)$$

$$7.1685 C_0 \cdot S \cdot t = C \cdot C_0 \cdot t \cdot t_1 + 7.1685 C \cdot S \cdot t - 7.1685 C \cdot S \cdot t_1$$

$$t_1 (C \cdot C_0 t - 7.1685 C \cdot S) = 7.1685 C_0 \cdot S \cdot t - 7.1685 C \cdot S \cdot t$$

$$t_1 = \frac{7.1685 \cdot S \cdot t (C_0 - C)}{C \cdot C_0 t - 7.1685 C \cdot S}$$

t_1 is the depth of water penetration in centimeters.

t_2 is the thickness of water-free dielectric in centimeters.

S is the area in centimeters of one plate of the capacitor.

t is the thickness of the coating in centimeters.

C_0 is the initial measured capacity in micro micro farads.

C is the present capacity of the capacitor.

C_1 is the series capacitor of water-saturated dielectric ($K_1 = 81$).

C_2 is the water-free series capacitor in micro micro farads.

Using the above equation, and several substituted values of capacitance between the initial capacitance C_0 and a final value when the depth of penetration t_1 is equal to the specimen thickness t , a graph of capacitance versus depth of penetration may be plotted, example, Figure 9. From this graph, for any measured value of capacitance, t_1 , the depth of penetration of water through this particular coating can be found.

Figure 10 shows a sample curve which in two weeks levels off at about 70 percent penetration. Such a curve is valuable in predicting life, ascertaining minimum film thickness for an application, and in evaluating the relative absorption characteristics of the coating system.

In addition to the use of water as an environmental contacting agent, various other electrolytes, varying in values of dielectric constant, conductivity, pH, osmotic pressure and other specific effects upon the coating may be used. The sample as shown, Figure 7, is particularly adaptable to the above investigations as well as for the study of the effects of galvanic phenomena such as polarity and cathodic currents. Anodes, cathodes and potential carrying electrodes are insertible within the electrolyte contained in the can.

Using this method for bituminous materials, it was found that in some cases several months are required to reach equilibrium. As shown in Figure 11, one sample required ten months. In most cases, much earlier predictions of coating life can be made. As shown in Figure 12, a group of the better bituminous materials was evaluated by this method for 400 days. At the end of this period, all samples were over 10^{14} ohms cm.³ in resistivity. The original thickness, t , the original dielectric constant, K , and the depth of penetration, t_1 , are shown. As with the gravimetric absorption method, t_1 varies in this group of samples. From this it can be concluded that coal tar and asphalt coatings, both hot- and cold-applied, are similarly satisfactory in this test.

Typical water penetration curves for hot-applied coal tar enamels are shown in Figure 13. Generally the higher plasticizer and pigment content of plasticized enamels cause greater water penetration values than for the standard enamels. Standard enamels or hard coal tar pitches may demonstrate cracking and thus show more erratic results.

Shown in Figure 14 are three water penetration curves for hot-applied asphalt coatings. It may be seen from such a curve as that for enamel G that a sufficient minimum mil film thickness specification must be considered in view of the depth of penetration and the rate of penetration increase with time. At 100 days, the water is saturated 25 mils into the sample and is increasing penetration at approximately three mils per year.

In Figure 15 three water penetration curves are shown for cold-applied asphalt and coal tar coatings demonstrating again that no great differences need exist between coal tar and asphalt coatings. At applied thicknesses double their penetration depth, the projected life of each, to a state of water-saturation, is a considerable period.

Where it is desired to combine bituminous materials such as a bitumen resin with epoxy resin and attain the necessary physical properties to permit thin coating applications, it becomes necessary to evaluate water penetration values to determine a minimum safe film thickness for satisfactory projected life. In Figure 16 is a bitumen-epoxy showing a projected life of approximately fifty years at 20 mils film thickness.

In order to study the smaller compounding effects produced by variations in types of pigment in the same base

formula of a bituminous coating, it is advantageous to combine the methods of gravimetric absorption and water penetration as in Figure 17. While all samples are over 10^{14} ohms cm.³ in resistivity, after 400 days some show increased leaching over others, and the capacitance penetration values can vary over 100%, a sensitive index to such compounding changes.

It was pointed out in the studies of gravimetric water absorption that higher temperatures (160°F) produce more rapid water absorption than is attained at room temperature. This same effect is noted as in Figure 18 when the capacitance method is employed. All samples failed within five weeks at 190°F.

In order to determine the electro-osmotic effect of applied potentials and their relation to water penetration by the capacitance method, several bituminous samples were subjected to water anodic potentials of 90 volts and 360 volts. The resultant curves are shown in Figure 19. Within three days the curves are well established. Early failures are predicted where resistivity values are relatively low, i.e., under 1×10^{12} ohms cm.³. Where resistivity values are high, i.e., over 1×10^{14} ohms cm.³, attenuation and equilibrium occur but at a faster rate than with no applied potential.

In review of the gravimetric water absorption and water penetration data obtained for bituminous materials, it appears that each method is a valuable tool for relatively short-term evaluation. By combining data, there is a definite relationship for a particular type of bituminous coating. Once this is established, either test may supplant or implement the

other. Figure 20 depicts the relationship for a bitumen-epoxy coating giving values for penetration and for 1,000-hour gravimetric absorption.

As in Figure 21, it is sometimes convenient to plot extended life in years using both the data obtained for weight absorption and capacitance penetration. Thus, one is able to determine a useful life based upon a specified initial film thickness application.

CATHODIC CURRENT DISBONDING TESTS

In addition to insulative coating evaluation by the methods described, it has become current practice to test insulative coatings immersed in electrolytes and subjected to cathodic potentials varying from less than one volt to several hundred volts. It is interesting to note that most workers have attempted to find a short-term cathodic current disbonding test for evaluating performance life of insulative coatings.

There are presently many variations of this type test being carried out. Higher voltages and currents and electrolytes of higher conductivities than are encountered in service are employed to produce fast breakdown. In general, it is difficult to recognize or control all of the factors contributing to coating breakdown. Some of the factors which we have found to be of importance are: (1) the pH values produced at the cathodes; (2) the applied potential; (3) the nature of the anode (Weast)¹¹; (4) the temperature; (5) the solution concentration and conductivity; (6) the type of surface preparation; (7) the type of primer; (8) the area exposed; (9) the electrical

resistivity value of the applied coating; and (10) the thickness of the sample.

Our cathodic current disbonding tests are generally carried out using entirely coated steel panels with waxed edges. A given area of panel is immersed in distilled water, tap water, or other more conductive electrolytes. While different anodes produce different pH values, we have found magnesium to be quite effective in producing high cathode pH values. Since magnesium is most commonly used in practice, we apply 1.5 volts D.C.⁺ to magnesium as the anode and 1.5 volts D.C.⁻ to the samples as cathodes. Small holes are drilled through the coatings to initiate areas of current flow. Initial current readings are taken and successive readings are made at daily intervals. When the coatings display a disrupted appearance, they are removed and the disbonded coatings are cut away to expose the entire bared area. This area is measured and can be related to current, potential and time.

In our work with cathodic current tests of bituminous materials, we have observed that thin films are readily disbonded. This is in accord with the fact that thin films are readily and quickly penetrated by water and electrolytes especially when migrating under potential stress. Tomashov et al.¹² have found that the coating itself can become cathodic, acting as a conductive film.

Cathodic disbonding susceptibility due to thinness is possibly due also to the factor of increased current flow at short-length pinholes in comparison to pinholes which are axially

long, even though the diameters of each are alike. The effect is explained by Sunde ¹³.

It is interesting to note that Koenecke¹⁴, who places coating specimens under anodic and cathodic stress and measures capacitance index (Shaw and Twiss)¹⁵, resistance, and disbonding, concludes that a basic film thickness must provide an insulating barrier under either test or service conditions to maintain electrical insulation and adhesion.

When cathode deposits occur at the coating, a thin film can be assumed to be highly saturated with alkalies which can react chemically to disintegrate many bituminous coatings. We have found the asphalt coatings generally to be more susceptible to high pH values than are coal tar materials (see Figure 6). In addition, both animal and vegetable residual pitches which are saponifiable by virtue of unsaturation or other reactive grouping are readily disintegrated in alkali at cathodes.

We have found that the proper metal surface preparation can effect up to several hundred percent increased cathodic current resistance to disbonding. Bituminous coatings over solvent-degreased steel panels disbond approximately five times the area of the same coatings over phosphated or grit-blasted steel. Almost as important as surface preparation is the use of proper primers.

Figure 22 was prepared to demonstrate a number of hot-applied bituminous coatings. Number 1 demonstrates the effect of a particularly good primer applied at 1 mil film thickness. The remaining samples shown without primers demonstrate the

relative resistance of each bituminous type. It can be noted that asphalts are generally more susceptible than coal tar types. Figure 23 shows a similar trend for the cold-applied bituminous coatings.

We have noted that a number of cold-applied type materials having very high values of volume resistivity, i.e., over 1×10^{14} ohms cm.³, tended to disbond more than certain cold-applied materials having much lesser values of resistivity. We have been able to establish that in some cases disbonding is accelerated in materials having very high volume resistivities. Note samples 9 and 10 in Figure 23. By adding 20% coal dust to bring the volume resistivity value from 1×10^{14} to 1×10^{11} ohms cm.³, the disbonded area of sample 10 was reduced to one-eighth that of sample 9. This accelerating effect is possibly due to insulation retention of higher potential differentials in local cathode cells formed at interfaces between bare and coated metal.

When compared to other conventional coating systems, the bituminous materials are highly resistant to cathodic current disbonding. All of the drying oils and oil-modified alkyds, epoxy esters, urethane esters and many vinyl type coatings are highly susceptible to cathode environments.

In Figure 24 the right panel is the same base bituminous asphalt as the left plus the addition of 10% fish oil and 10% zinc chromate. With these additions the asphalt is highly degraded and is readily disbonded.

In Figure 25 the left panel is 20% alkyd and 80% asphalt. The right panel is 100% asphalt.

In Figure 26 the left panel has no primer and the right panel is primed with an iron oxide alkyd primer. The coating is refined cold-applied asphalt mastic. Increased susceptibility to disbonding is noted in the primed panel.

In Figure 27 disbonding due to pigment reactivity is demonstrated. The same base asphalt cold-applied coating is pigmented with glass fibers on the left and with asbestos fibers on the right. The glass is subject to attack by the alkali present.

CONCLUSIONS

The evaluation of long-term performance types of bituminous coatings is possible in the laboratory, based upon laboratory test procedures being considered and established in terms of normal-range exposures.

Water, the single most important factor in the excellent performance life of bituminous coatings, is absorbed by osmotic and electro-osmotic effects. The absorption may be measured gravimetrically and related to quantity per unit area. By this method, also, the solubility or leaching characteristics of certain bitumens may be detected by means of drying and weighing samples after water immersion exposures. Coal tar types were found to be more susceptible than asphalts in this regard. In gravimetric absorption tests carried out at 160°F, this fact was accentuated. At 160°F all of the bituminous materials tested showed multifold absorption increases.

Electrical properties have been studied in relation to water absorption characteristics and to the performance of

bituminous materials as insulative coatings. The bituminous coatings have volume resistivities in the range of 1×10^{12} to 1×10^{15} . It was found that volume resistivity measurements alone do not lend themselves to short-term evaluation methods.

Using bituminous coatings, a new method was developed to derive measurements of depth of water penetration by electrical capacitance. This method permits evaluation of bituminous compounds of known performance against newer compounds. Water penetration values can be co-related to gravimetric absorption. This method permits projected life studies of coatings and permits safe film thickness specifications for new compounds. The method is fast, non-destructive and sufficiently sensitive to detect small changes in exposure conditions or compounding ingredients. It is an effective short-term test giving projected values for the long-life bituminous coatings, well within a 400-day test period. The philosophy of a short-term rather than an accelerated test is preserved.

In applying accelerated test methods such as the cathodic current disbonding test to bituminous materials, it was found that there can be many factors which affect the results obtained. Using a moderate version of the cathodic current disbonding procedure, a number of bituminous materials were evaluated and were found to be, in general, superior to many other coating types.

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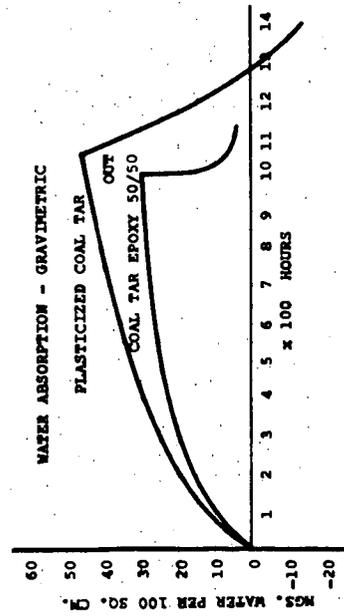


Fig. 1

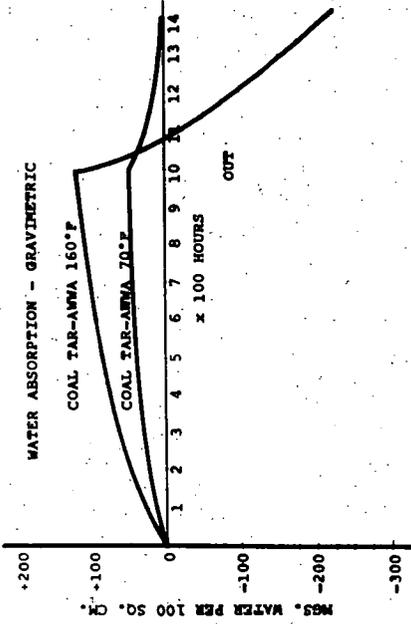


Fig. 3

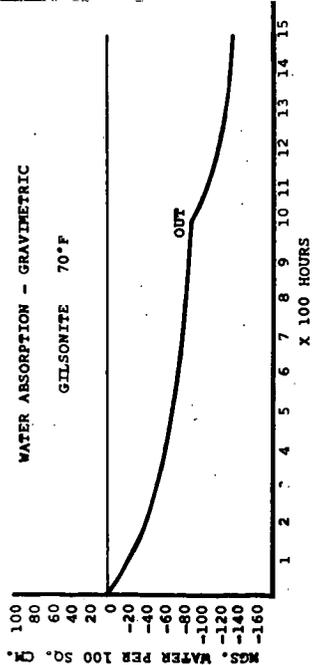


Fig. 2

WATER ABSORPTION - GRAVIMETRIC

MGS. PER 100 SQ. CM. PER 1000 HOURS IMMERSION - TAP WATER
VOLUME RESISTIVITY = 70000 (OHMS)

TYPE	MG. GAIN		LOSE ON	
	AT 70°F	LOSE ON DRYING	AT 160°F	LOSE ON DRYING
ASPHALT M 220°F (HOT-APPLIED)	30	0.0	—	—
ASPHALT SOLUTION 240°F (COLD-APPLIED)	33	0.0	—	—
ASPHALT OXIDIZED ALIPHATIC 200°F (HOT-APPLIED)	36	0.0	156.00	0.00
ASPHALT OXIDIZED ALIPHATIC 230°F (HOT-APPLIED)	39	0.0	186.00	0.00
ASPHALT OXIDIZED ALIPHATIC 260°F (HOT-APPLIED)	39	0.0	270.00	0.00
COAL TAR PLASTICIZED ENAMEL AWMA (HOT-APPLIED)	40	5.0	120.00	-346.00
COAL TAR STANDARD ENAMEL PITCH (HOT-APPLIED)	40	-7.0	—	-187.00
ASPHALT-STYRENE (COLD-APPLIED)	40	0.0	438.00	—
ASPHALT PIPELINE ENAMEL 4	40	0.0	—	—
MYLAR (POLYESTER) PRE-FORMED FILM	41	0.0	—	—
COAL TAR PLASTICIZED ENAMEL (HOT-APPLIED)	42	-13.0	930.00	-774.00
ASPHALT S 220°F (HOT-APPLIED)	44	0.0	1852.00	0.00
ASPHALT K 220°F (HOT-APPLIED)	49	0.0	533.00	0.00
ASPHALT R 220°F (HOT-APPLIED)	55	0.0	270.00	0.00
ASPHALT (REFINED) COATING 240°F (COLD-APPLIED)	64	0.0	702.00	0.00
COAL TAR EPOXY (AMINE CURE) 70°F CURE	76	-19.0	-81.00	-200.00
COAL TAR-NITRILE COATING (COLD-APPLIED)	83	-7.0	3800.00	-433.00
COAL TAR MASTIC CA-50 (COLD-APPLIED)	107	-208.0	1400.00	-730.00

Fig. 4



Fig. 7

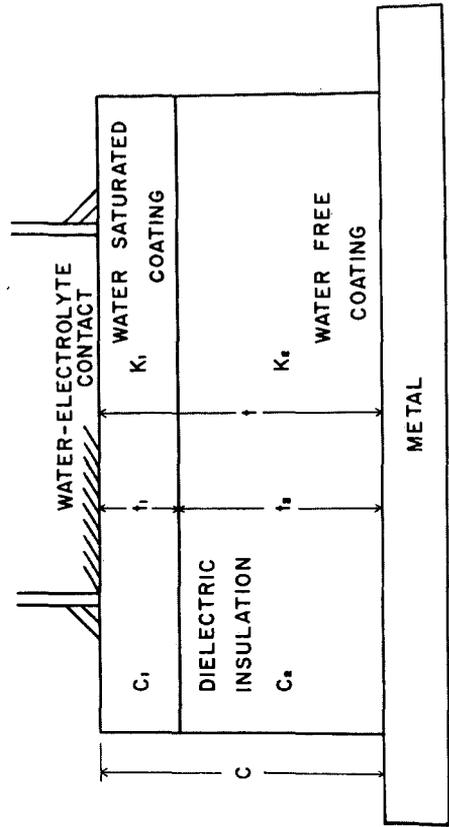


Fig. 8

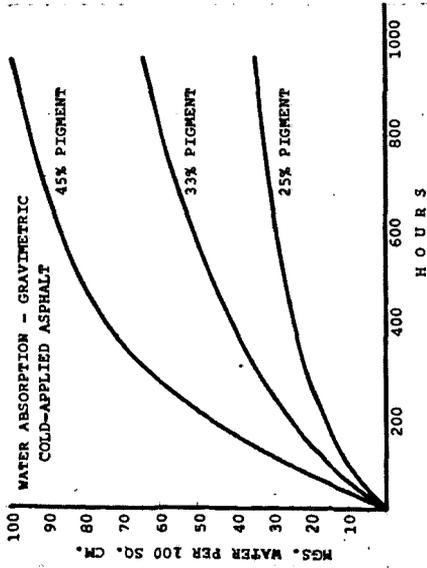


Fig. 5

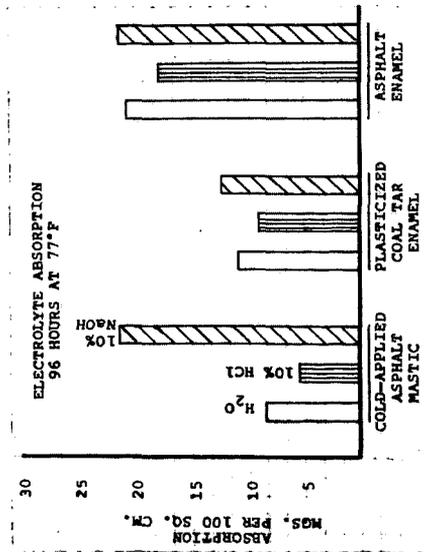


Fig. 6

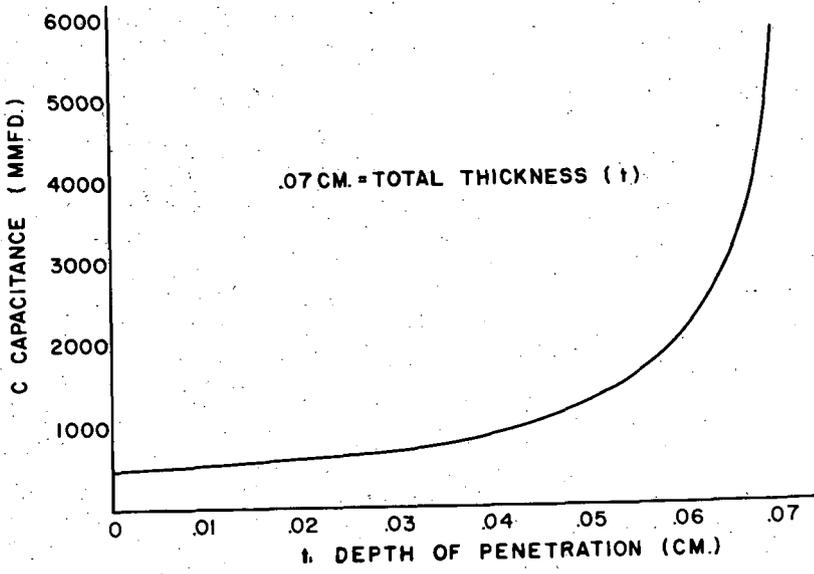


Fig. 9

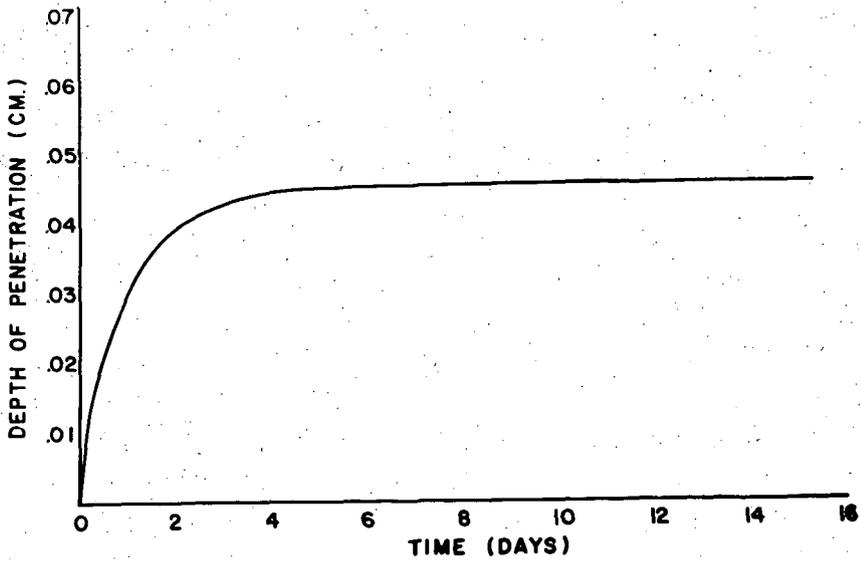


Fig. 10

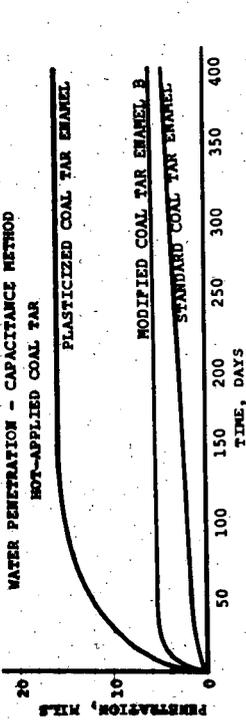


Fig. 13

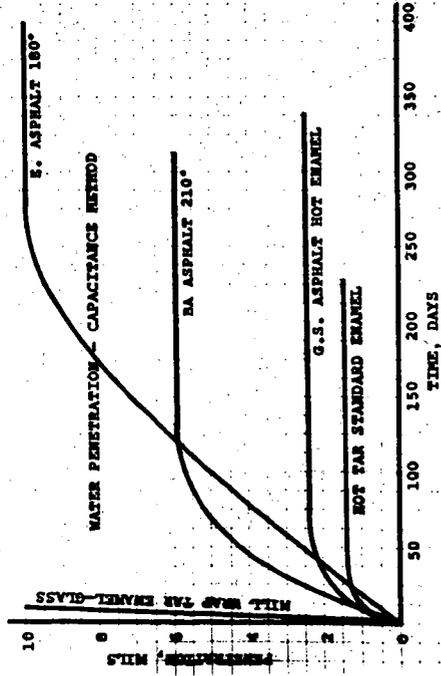


Fig. 11

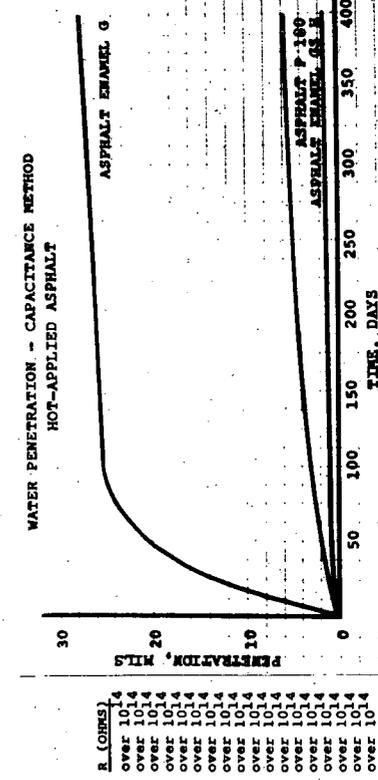


Fig. 14

WATER PENETRATION - CAPACITANCE METHOD

400 DAYS - 70°F WATER - VOLUME RESISTIVITY 70000 OHMS

TYPE	t (MILS)	k (K)	ε ₁ (MILS)	R (OHMS)
ASPHALT M 220°F (HOT-APPLIED)	18	3.89	2.00	over 10 ¹⁴
ASPHALT SOLUTION 240°F (COLD-APPLIED)	24	4.92	4.92	over 10 ¹⁴
ASPHALT OXIDIZED ALIPHATIC 200°F (HOT-APPLIED)	31	8.54	1.50	over 10 ¹⁴
ASPHALT OXIDIZED ALIPHATIC 230°F (HOT-APPLIED)	35	8.68	1.50	over 10 ¹⁴
COAL TAR PLASTITIZED ENAMEL AWMA (HOT-APPLIED)	73	14.23	6.00	over 10 ¹⁴
COAL TAR STANDARD ENAMEL PITCH	38	3.90	8.00	over 10 ¹⁴
ASPHALT-STYRENE (COLD-APPLIED)	26	7.50	6.00	over 10 ¹⁴
ASPHALT PIPE ENAMEL 4 (HOT-APPLIED)	39	10.95	1.00	over 10 ¹⁴
COAL TAR PLASTITIZED ENAMEL (HOT-APPLIED)	70	9.40	16.00	over 10 ¹⁴
ASPHALT S 220°F (HOT-APPLIED)	106	7.40	2.00	over 10 ¹⁴
ASPHALT H 220°F (HOT-APPLIED)	185	8.75	2.80	over 10 ¹⁴
ASPHALT (REFINED) COATING (COLD-APPLIED)	165	5.49	3.20	over 10 ¹⁴
ASPHALT (REFINED) COATING (COLD-APPLIED)	12	17.30	4.80	over 10 ¹⁴
COAL TAR-EPOXY AMINE CURE (COLD-APPLIED)	20	6.40	4.00	over 10 ¹⁴
COAL TAR-NITRILE COATING (COLD-APPLIED)	25	8.26	6.75	over 10 ¹⁴
COAL TAR MASTIC CA-50 (COLD-APPLIED)	31	9.00	17.00	over 10 ¹⁴

Fig. 12

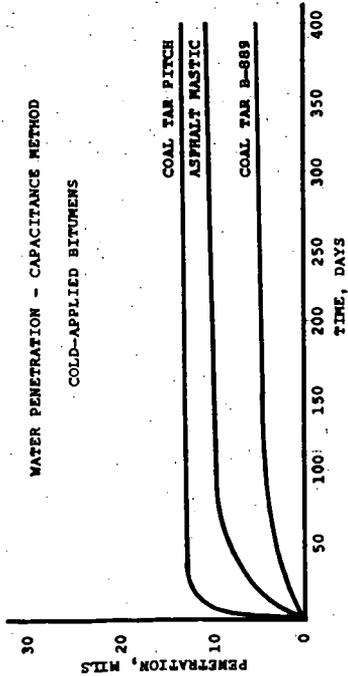


Fig. 15

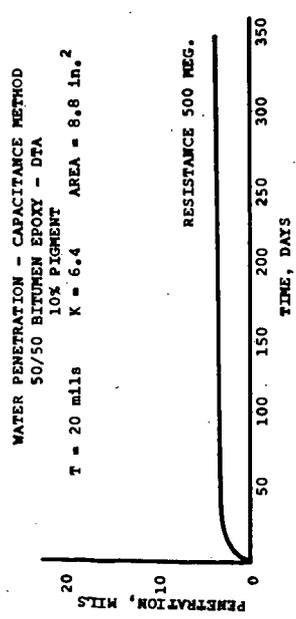


Fig. 16

WATER ABSORPTION - GRAVIMETRIC
WATER PENETRATION - CAPACITANCE METHOD

USING A COMMON BASE FORMULA - REFINED ASPHALT
(COLD-APPLIED) AND VARYING PIGMENT TYPES
(35% PIGMENT)

FORMULA	MGS. GAIN PER 100 SQ. CM. PER 1000 HOURS	MGS. LOSS ON DRYING	ϵ (MILS)	(K)	VOLUME R.	t_1 (MILS) PENETRATION
B-909	22.0	-17	22	9.18	over 10^{14}	5.50
B-910	23.0	-20	27	10.40	over 10^{14}	7.60
B-911	19.0	-42	18	8.24	over 10^{14}	5.50
B-912	15.7	-39	23	7.92	over 10^{14}	10.70
B-913	15.6	-50	22	9.87	over 10^{14}	7.10
B-914	9.5	-54	25	8.05	over 10^{14}	11.70
B-915	47.0	-53	24	8.48	over 10^{14}	12.20
B-916	37.0	-51	20	9.97	over 10^{14}	6.70
B-917	-12.0	-82	24	10.56	over 10^{14}	8.05
B-918	11.0	-53	23	10.63	over 10^{14}	6.80

Fig. 17

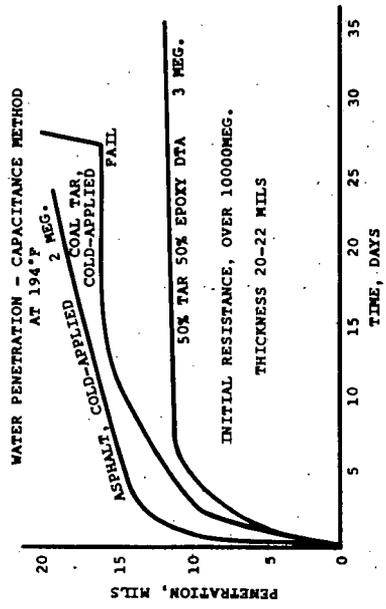


Fig. 18

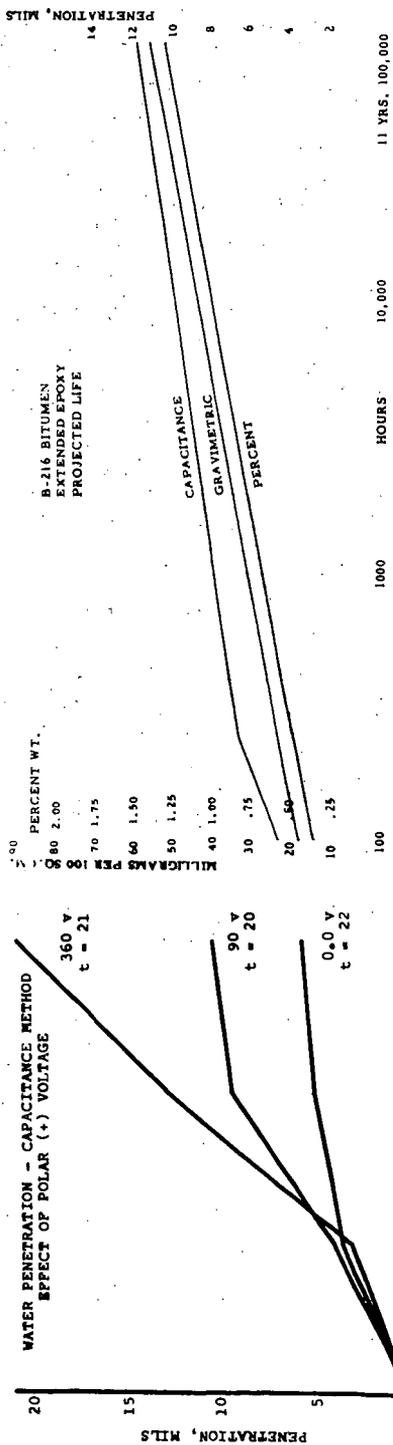


Fig. 19

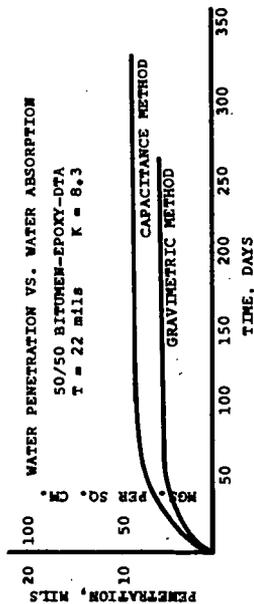


Fig. 20

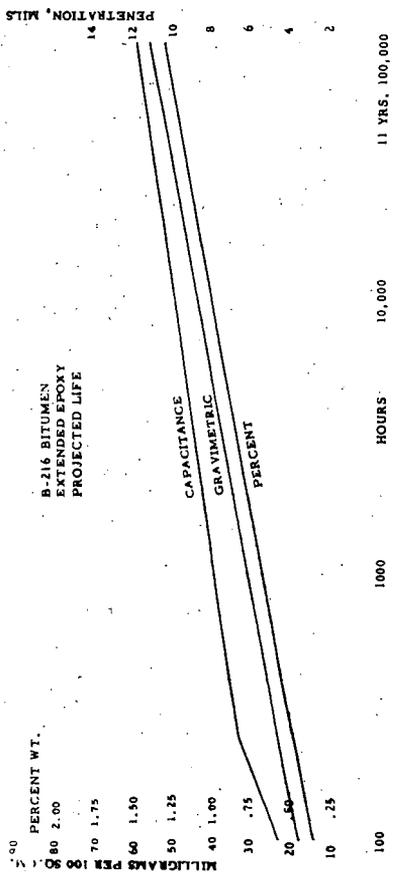


Fig. 21

CATHODIC CURRENT DISBONDING TESTS

COATED 2 X 4 INCH PANELS IMMERSED 2 1/2" IN 70000 OHMS, R, WATER, 12 CM. FROM MG. ANODE, 1.5 VOLT CLOSED CIRCUIT POTENTIAL, 1/16" PINHOLE THROUGH PANEL IN SOLUTION.

COATINGS (HOT APPLIED)	DISBONDED AREA SQ. M.M.
1. ACRYLIC PRIMER + PLASTICIZED COAL TAR ENAMEL	1.0
2. MODIFIED COAL TAR ENAMEL (NO PRIMER)	56.0
3. COAL TAR STD. ENAMEL PITCH	144.0
4. ASPHALT (OXIDIZED ALIPHATIC)	380.0
5. COAL TAR STANDARD ENAMEL	500.0
6. WURTZELITE ASPHALT	621.0
7. COAL TAR PLASTICIZED ENAMEL A.W.W.A.	800.0
8. COTTONSEED PITCH BITUMEN	1,254.0
9. ASPHALT (230°F. ALIPHATIC)	2,250.0
10. ASPHALT (BLOWN) 220°F.	3,500.0
11. ASPHALT PIPE ENAMEL	3,500.0
12. ASPHALT (PALM OIL PITCH)	3,500.0

Fig. 22

CATHODIC CURRENT DISBONDING TESTS

COATED 2 X 4 INCH PANELS IMMERSED 2½" IN 70000 OHMS,
R, WATER, 12 CM. FROM MG. ANODE, 1.5 VOLT CLOSED
CIRCUIT POTENTIAL, 1/16" PINHOLE THROUGH PANEL IN
SOLUTION.

THICKNESS RANGE, 17 - 35 MILS

COATINGS (COLD APPLIED) (NO PRIMERS)	DISBONDED AREA SQ. M.M.
1. COAL TAR MASTIC CA-50 TYPE	64.0
2. COAL TAR MASTIC " " "	100.0
3. COAL TAR EPOXY (D.T.A.)	100.0
4. COAL TAR NITRILE COATING	440.0
5. COAL TAR-EPOXY (POLYAMINE CURE)	1,575.0
6. ASPHALT - STYRENE	3,000.0
7. ASPHALT - REFINED	3,500.0
8. ASPHALTIC RESIN PRIMER + ASPHALTIC BITUMINOUS TAPE	3,500.0
9. COAL TAR NITRILE (C-37)	700.0
10. C-37 + 20% COAL DUST	56.0

Fig. 23

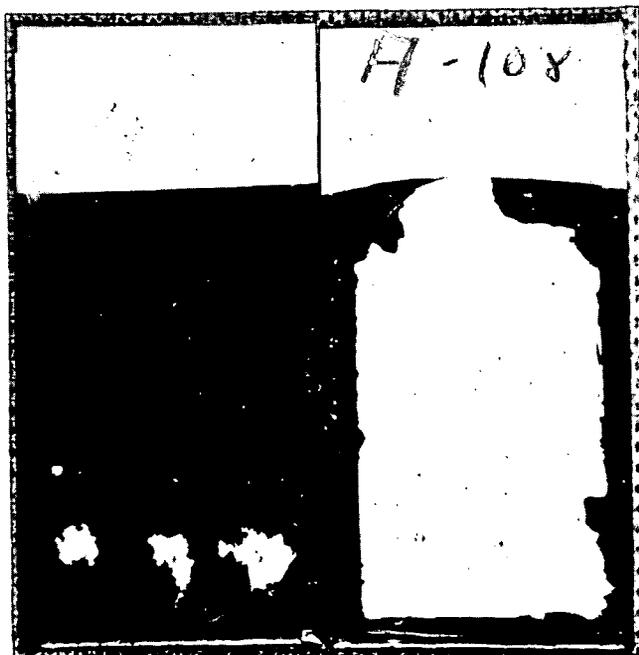


Fig. 24

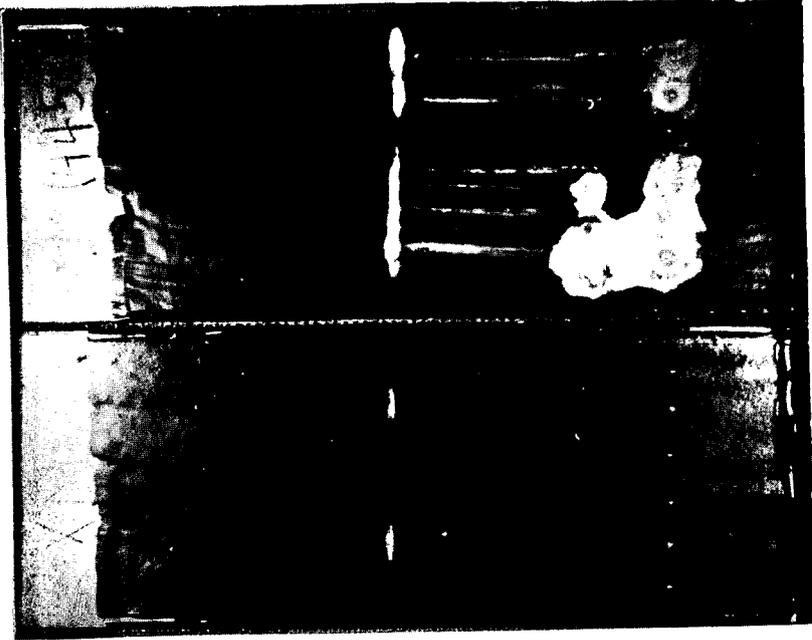


Fig. 26

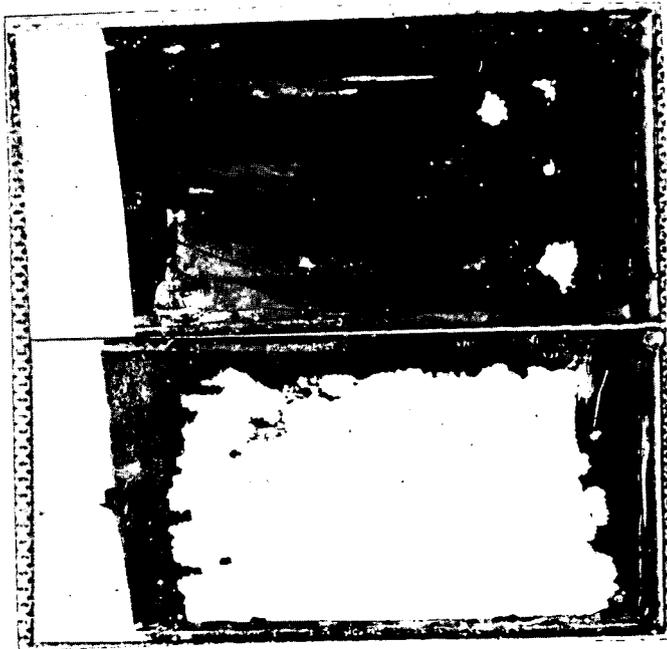


Fig. 25

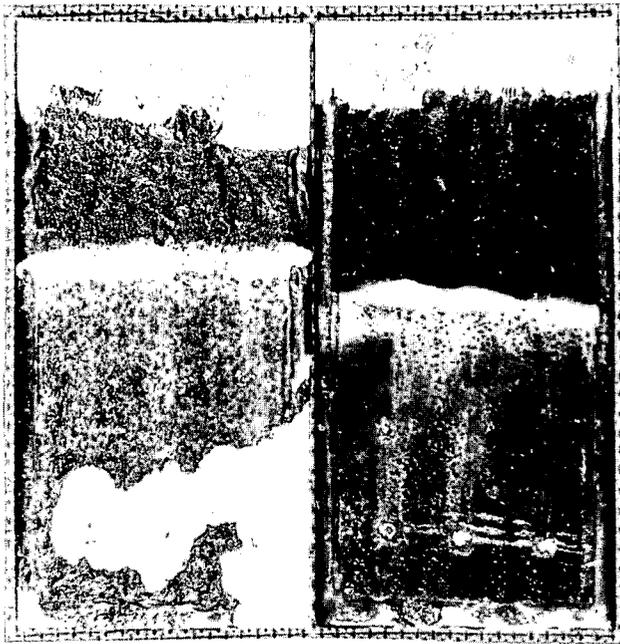


Fig. 27.

ENVIRONMENTAL TESTING

OF

BITUMINOUS COATINGS

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INTRODUCTION

The topic of environmental testing of bituminous coatings covers a broad spectrum of test procedures and materials. As referred to in this paper, environmental testing includes utilization of both natural and artificial environments in testing programs other than in-service testing. The term "Bituminous Coatings" applies to coatings directly derived from petroleums, coal-tars and gilsonite. The environments of concern include atmosphere, water (both fresh and sea water) and soils.

PURPOSE OF ENVIRONMENTAL TESTINGS

Each environmental test program must first take into account the purpose for conducting the tests, so that reasonable objectives may be established. Let us first consider some of the purposes that could motivate a test program.

Production Quality Control: This is probably the least frequently encountered reason for an environmental test program, because there are very few environmental tests that yield data quickly enough to be of use in controlling production quality. One applicator of protective coating for underground piping does utilize such a test in his mill. A number of samples of coated pipe are cut out of each production run. This run is not released from the mill until the samples are tested in a salt water solution, under cathodic protection for a 24 - 48 hour period. Disbonding of the coating due to the cathodic protection must not exceed certain limits set up by the applicator. We are not completely convinced of the value of this procedure, due to its highly artificial environmental conditions, but it does represent an effort to control the end-quality of the product through an environmental testing procedure.

Aid in the Development of a New Or Modified Product: As in the previously described case, here we are faced with the pressure of attaining results susceptible to evaluation in as short a time as possible. Frequently, attempts to "accelerate" effects of environments leads to the development of extremely severe artificial environments. Unfortunately, the intensification of one or more environmental factors does not produce the same short-term effects as a less intense factor operating over a longer period of time. This necessitates that such tests be developed with care, and that their results be interpreted knowingly. Obviously, however, each new development can not be evaluated by full-term natural environmental testing. Intensified testing will be used, sometimes yielding data of great value, other times misleading the investigator. Such tests may, however, be utilized to determine weak points in a coating material and help determine if changes in formulation strengthen the weak points.

Substantiation of Sales Claims: This motivation leads frequently to somewhat less than objective testing, but must be mentioned because of the prevalence of test programs that originate from this need. There is no lack of ethics in providing the sales department with data from environmental tests that demonstrate the good qualities of a particular product. Unfortunately, on some occasions, researchers have destroyed their credibility by over-attention to a products strong points - or to a competing products weak points. This can lead to widespread indifference to what may be excellent data, because the investigator, no matter how highly placed, is suspected of lack of objectivity.

Compliance with Government or Other Purchaser's

Specifications: Environmental test programs of this nature effectively tie the hands of the investigator. The widespread dependence of some governmental agencies, in the past, upon specific environmental tests, that at times were not related to end-usage of the protective coating led to widespread hostility to certain environmental tests. This does not reflect on the validity of the tests, but emphasizes the importance of proper selection of tests and knowledgeable interpretation of their results.

Selection of a Coating for a Specific Need: The remainder of this paper will be devoted to exploring the use of environmental testing for this purpose.

ATMOSPHERIC ENVIRONMENT

Laboratory Testing: A number of procedures are available for laboratory evaluation of coatings. Most of these tests utilize artificial sources of radiation to simulate sunlight and fog chamber devices utilizing high humidity atmospheres and/or periodic spraying with water. ASTM Standard D529-62 "Accelerated Weathering Test of Bituminous Materials" covers the operation of light-and-water-exposure apparatus for the exposure of bituminous roofing and waterproofing materials having a minimum softening point of 200°F. These procedures utilize an enclosed carbon-arc lamp and a water spray apparatus.

While use of this apparatus will result in more rapid coating deterioration than found in natural environments, there is no reliable means of equating the time of artificial exposure to failure to the time of natural exposure to failure.

It is quite possible to arrive at substantial difference endurance rankings utilizing the "accelerated" test from that which would be arrived at under a natural environment.

Modification of this procedure by use of a xenon-arc type apparatus has yielded more meaningful data according to Martin⁽¹⁾ who compared carbon-arc, xenon-arc and natural radiation. Martin utilized microtechniques to increase the sensitivity of evaluation of asphalt degradation by use of the change in absorbance of the carbonyl functional groups. He found that his ranking of degradation as obtained by use of the xenon-arc compared directly with the ranking obtained by use of natural exposure to sunlight with radiation monitored by the Eppley pyroheliometer. He found discrepancies between these rankings and those obtained by the use of the carbon-arc. These observations, together with his demonstration of the use of microtechniques seem to be major contributions.

While the use of weatherometer-type apparatus has its limitations, careful evaluation of its results can be utilized to separate material with gross differences in weathering resistance qualities.

Others have used arbitrary laboratory tests to furnish at least data that will provide a basis for a rough weeding of obviously inferior materials. Flournoy⁽²⁾ suggests a method for this purpose. He utilizes three tests, as follows:

1. Thickness: Minimum of 0.005-inch for corrosive atmospheres.
2. Flaws and Holidays: Electrical resistance of a coated 4-inch by 2-inch panel must be at least initially 1,000,000 ohms and must be at least 750,000 ohms after 24 hours of water immersion.
3. Flexibility: The test panel, after being bent 90° around a 1-inch diameter rod must have no obvious coating failures and must retain an electrical resistance of 750,000 ohms.

This presents rather arbitrary criteria that may be applicable to certain circumstances. The rather short term environmental test, immersing the test coupon in water could give a rough idea of initial coating condition, but a 24-hour test seems of little use other than to eliminate coatings that were very obviously inferior. Undoubtedly, arbitrary tests of this nature could be of significant value in specific

instances, but would be of little general use.

Natural Environment Tests: Exposure to a natural environment seems to be the best method of environmental testing of coatings for atmospheric exposure conditions. The major disadvantage seems to be that the time required for a full evaluation can be excessive, and that there is some difficulty in knowing exactly to what factors the panels have been exposed. Caryl⁽³⁾ suggests the use of mirrors to increase the intensity of solar radiation, together with a rotating mount that keeps the panels always facing the sun, both with and without periodic washing with distilled water. His studies indicated that this system could give failures in 14 weeks that would occur only after 3 years at a 45° south exposure.

Others utilize special panels with angles, crevices, rivet heads, weld splatter and other severe surfaces to subject the coatings to the most difficult areas to coat, thereby providing a panel with conditions that lead to early failures in actual service. This type panel has considerable merit and can lead to early elimination of inferior coatings. The evaluation of coating conditions on panels such as this is more complicated and time-consuming than that of flat panels, but the data obtained can be of corresponding higher value.

Of course, natural environments vary substantially from location to location and indeed over a wide range of any given location. This necessitates methods of evaluating the environmental effects to which a coating has been subjected over its test period.

Solar radiation is one factor of major concern. The evaluation of this factor is relatively simple and can be accomplished by the use of the Eppley Pyroheliometer and appropriate recording and integrating devices. Generally, records are kept of total langleys, langleys over .823, and hours of radiation over .823. Martin demonstrated a close correlation between total langleys and asphalt oxidation. The pyroheliometer, together with further development of microtechniques, seems to offer a path for very meaningful, relatively short-term evaluations, utilizing natural sunlight.

Other factors of major importance are temperature ranges relative humidity, and any atmospheric pollutants that may be of major importance. Continuous recording of temperature and humidity are essential. Methods also have been devised to monitor sulfides in the atmosphere.

UNDERGROUND AND UNDERWATER EXPOSURE

The success of underground and underwater exposed bituminous coatings or any coating requires qualities not absolutely necessary for atmospheric exposed coatings. These environmental conditions impose the necessity for greater physical strength, higher electrical resistance, and usually require much longer useful life than atmospherically exposed coatings. These requirements vary according to the end-usage of the product and to economic considerations. Coatings for corrugated galvanized steel storm sewers do not have to meet the rigid requirements applied to coatings used on thin-wall high pressure gas and oil pipelines. Any environmental testing program must, therefore, fully consider the end-usage of the materials tested. For purposes of further discussion, we will consider only those applications where the minimum length of coating effectiveness is required to be in excess of 30 years.

Laboratory Tests: The U. S. Department of Reclamation⁽⁴⁾ utilizes a series of tests to evaluate coatings for use in submerged service. These tests include: Fresh water immersion⁽⁵⁾; salt spray box⁽⁶⁾; outdoor weathering exposure⁽⁷⁾; and weatherometer⁽⁸⁾. In cases where specific problems exist, the Bureau designs specific tests.

While there have been a few standards developed for the evaluation of the quality of certain specific bituminous coatings, we lack standardization of tests for comparing performances of various coatings to each other. Generally, investigators develop their own tests and procedures in much the same manner that the Bureau of Reclamation has done. It appears that this situation will not change in the immediate future.

Let us consider, therefore, the development of a test program to evaluate the relative merits of protective coatings for underground structures, with the understanding that a good coating must perform well for at least 30 years. The

structure to which the coatings is to be applied might possibly be cathodically protected.

Usually the investigator is faced with a vast array of proposed coatings. His first problem then is the development of a method for "weeding" the grossly inferior materials from those that may possess some merit. The judgment of an experienced investigator generally is the fastest "weeding" mechanism; however, he most frequently must substantiate his judgment with test data.

The "salt-crock" test, or a modification of it, most generally is applied to this stage of the investigations. While there are infinite variations of this test, it consists essentially of placing a coated specimen in a container of salt water. The electrical resistance between the sample and a fixed electrode is then measured; the measured resistance must exceed an arbitrary value to qualify the coating for further consideration, and must continue to maintain an arbitrary minimum resistance over an equally arbitrary period of time. The duration of this test is generally short, in the order of 3 - 6 months. In some cases the sample is maintained electrically negative to the solution in which it is immersed in order to get some evaluation of its performance on a cathodically protected structure.

As a preliminary "weeding" test, the salt-crock test has considerable merit. There are many factors that can lead to erroneous results, however. Certain coatings can not readily be applied to small coupons. For example, a heavy asphalt-mastic pipe coating applied by hand has substantially different qualities from the same material extruded on pipe by commercial machinery. A hand-applied sample could be expected to fail in a shorter period of time than a machine-applied coating. Conversely, some other coatings have much better qualities when hand-applied than they would when applied on a commercial scale. A short-term salt-crock test would reveal inherent porosity in a coating, but would not, in six months, necessarily show a tendency for moisture absorption that could lead to failure in 5 - 10 years. There is also the hazard that electrical connections to the sample might be difficult to coat and electrical leakage caused by the connection could lead to erroneous results.

One method of conducting a salt-crock test may be of some interest. A standard procedure adopted by the author's company uses a coated pipe sample, preferably with the

coating applied by the same equipment used to apply the particular coating on a commercial scale. The sample is selected so that no accidental flaws exist. The coated sample, generally about 18 inches in length, is placed concentrically in a second uncoated pipe of a convenient larger size. Generally, a 3/4-inch diameter sample would be placed in a 2-inch pipe. A rubber stopper the size of the casing pipe is cut so that the sample will fit snugly in it. The assembly is then made as shown in Fig. 1, with the space between sample and pipe being filled with water made highly conductive by adding salt. The electrical resistance between sample and casing is used as a measure of the coating effectiveness. High quality coatings will maintain resistances of in excess of 1,000 megohms per square foot of surface area for long periods of time.

If a value of about 10 megohms per square foot is used as a criterion, most grossly inferior coatings will be detected in a few weeks time, and can be eliminated from further testing. Higher quality coatings can be maintained in this test for extended periods of time to give information regarding long-term moisture absorption and performance under cathodic protection conditions.

The decision to give further consideration to a given coating that performed well in the salt-crock test must also consider the physical requirements for the coating. Resistance to impact, shock and sustained loads must be determined by appropriate testing. Resistance to underfilm water migration should be evaluated by the use of samples with scratched or impacted areas. The salt-crock test can be used for this evaluation, although electrical resistance measurements, since the underfilm-migration path may itself be high in electrical resistance. Generally, this test is conducted both with and without cathodic protection. The cathodically protected samples would be affected by the physical pressure of liberated gasses and high pH conditions at the pipe surface. The use of unrealistically high voltages for this test could yield very misleading data.

Coatings surviving the above tests can next be considered for further testing in environments simulating, as close as possible, those conditions that will be encountered in service. Engineering judgment may also lead to the beginning of in-service testing at this time. Where service conditions are such that high soil stress conditions may be expected, tests specifically designed to evaluate soil stress conditions

may be used. Samples can be placed in a bentonite environment that is alternately wetted and dried. The performance of the coating can be evaluated electrically by measurement of the resistance between the sample and a ground reference. This would be supplemented by physical examination at the end of the test period or when electrical measurements indicated that failure had occurred.

This method of testing seems to be worthwhile only if extreme soil stress conditions are expected. Otherwise coatings that might perform well, and economically, under actual service conditions may be unwisely eliminated.

Natural Environment Tests: Where possible, it seems best to test the coatings under conditions as close as possible to those encountered in service. One approach is to use an outdoor test box filled with soil typical of the area. Such an arrangement is shown in Fig. 2. A permanent box is constructed outdoors. An aluminum foil lining is placed in the bottom of the box. Test samples are inserted through sleeves in the box, with plastic casing spacers on the samples where they pass through the sleeves. Standard rubber casing end seals are then used to seal the space between sample and sleeve. The box is then carefully filled with the selected soil. The coating extends to the ends of the pipe samples. Stainless steel guard rings are clamped on the pipe about 6 inches outside the casing seals. If the coating includes glass fabric or felt, the guard ring must be in contact with the bottom layer of felt or glass fabric. These rings have to be installed very carefully, and are essential to reliable readings.

Use of a soil box such as this simplifies electrical measurements and keeps the samples relatively accessible for physical examination. The shallow nature of the box causes the samples to be exposed to more severe wetting-drying and temperature cycles than would be experienced under service conditions. If grass is allowed to grow in the soil, the effects of roots would also be more severe. These factors must be weighed in evaluating test results. In one 7-year test, the electrical resistance of high quality coatings was in excess of 50 megohms per square foot.

Another approach would be to bury samples directly in a typical environment. If the entire sample is buried in this manner, great care must be taken to assure that the pipe ends and electrical connections are coated at least as well as the sample

coating. This can prove to be very difficult. One arrangement is shown on Fig. 3. The most critical factor is the encapsulation of the ends and connections. As long as this is effective, the resistance between the guard rings and earth will be extremely high - any leakage of water into the encapsulation will be detected by a change in the guard ring resistance to earth. Of course it is essential that the test wire insulation be perfect. While this test is probably the most difficult to set up properly, its long-term results are probably the most meaningful.

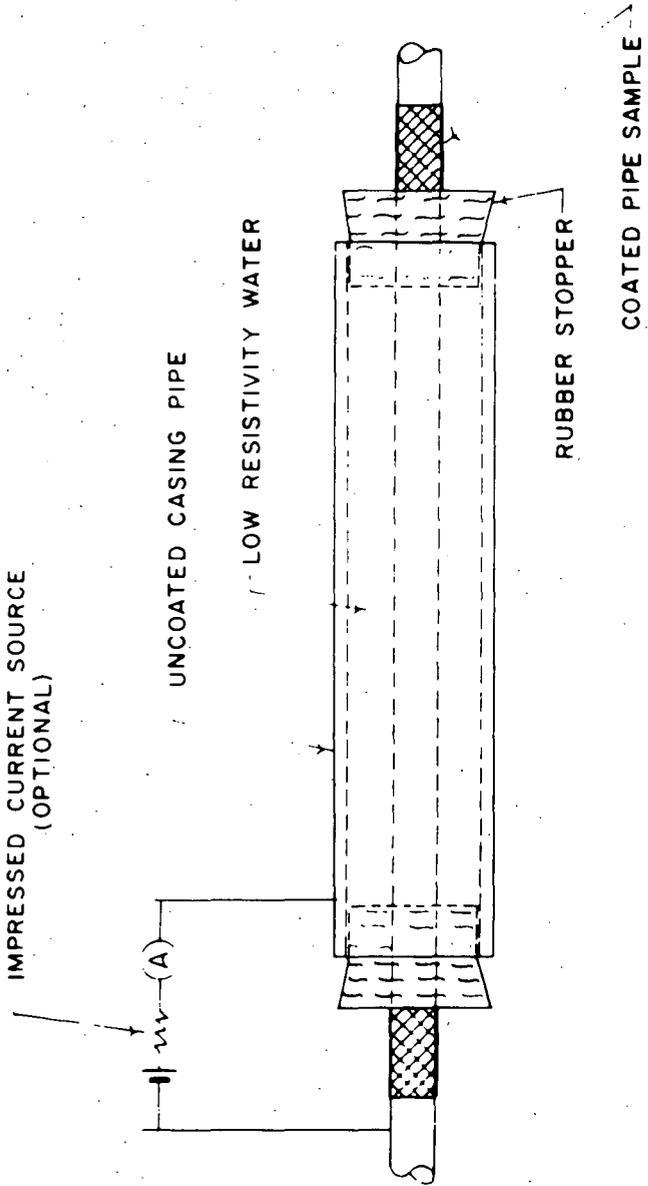
Perhaps the largest scale natural environmental test program for protection coatings was conducted by the American Petroleum Institute⁽⁹⁾. These tests utilized 16 test sites and involved different coating systems applied to 3-inch pipe at each of the test sites. There were also 19 coatings applied to 14 working pipelines. The test program was of about ten years' duration ending in 1940. Great progress has been made in underground protective coatings since the test started in 1930, but unfortunately the tests were not continued to include new coating developments. While the results of this program are not directly applicable to today's problems, the program itself is of interest and could be used as a starting point for the resumption of similar industry-wide tests.

SUMMARY

Environmental testing of bituminous coatings can provide valuable information. Extreme caution must be exercised in the use and interpretation of "accelerated" tests. Coordination of "Environmental Testing" and "In-Service" testing is essential to the intelligent solution to coating problems.

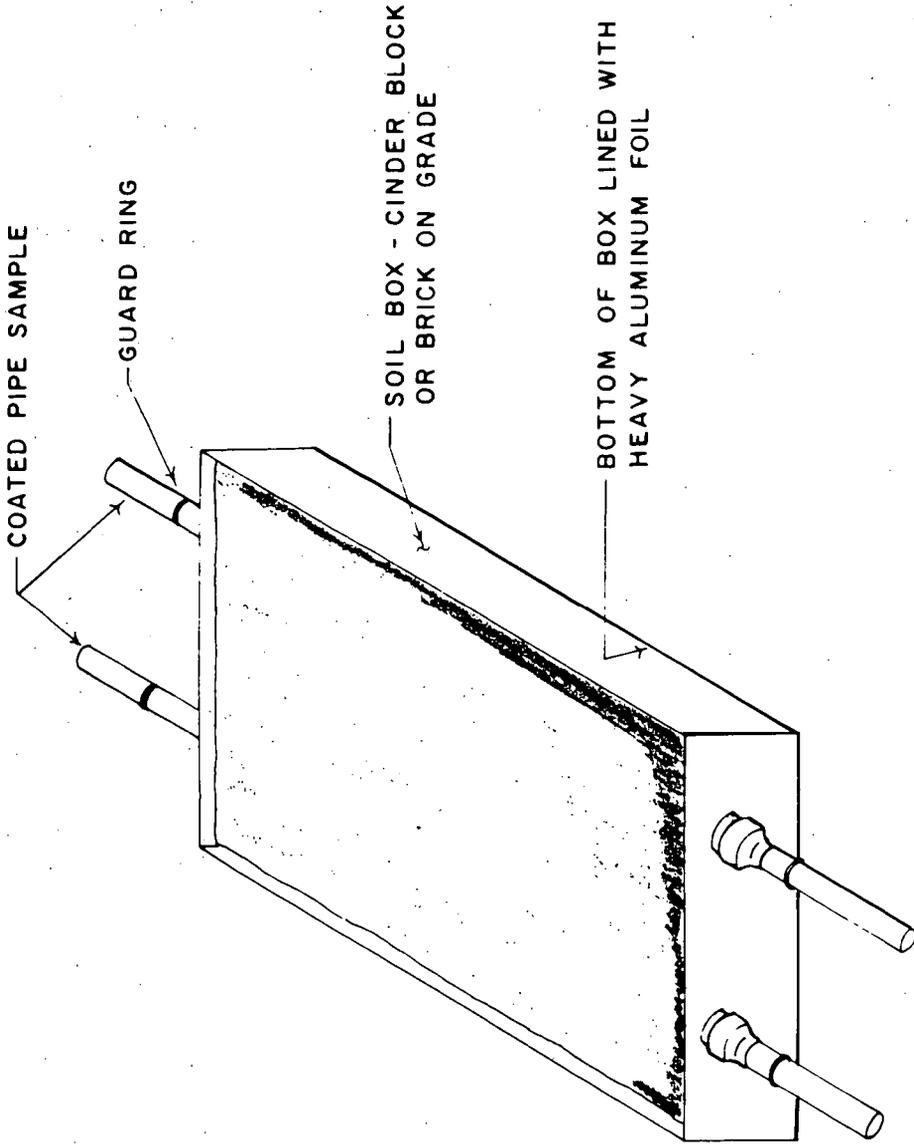
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MODIFIED SALT-CROCK TEST

FIGURE 1



CONTROLLED SOIL ENVIRONMENT TEST

FIGURE 2

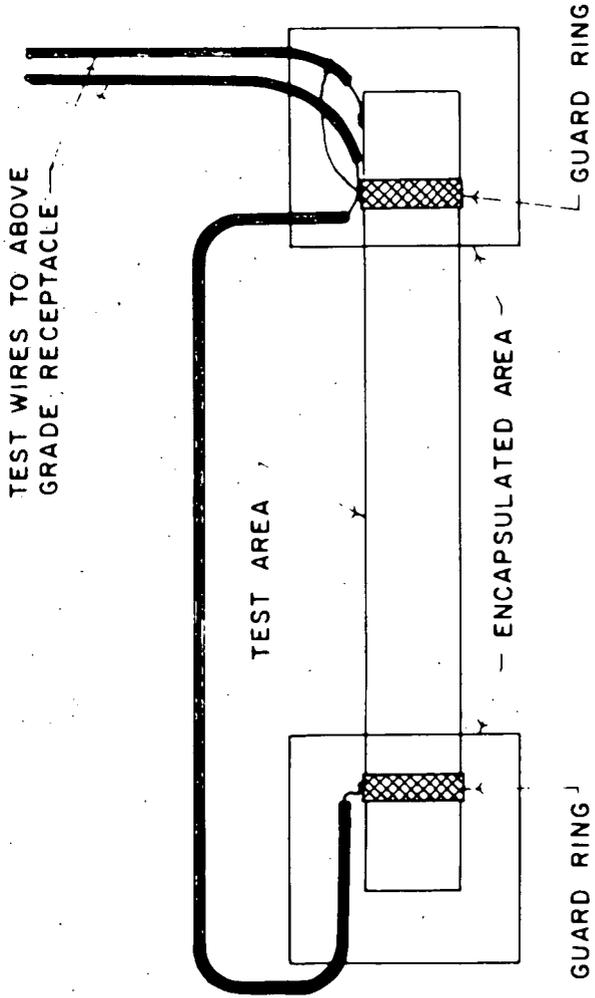


FIGURE 3

SERVICE TESTING OF BITUMINOUS COATINGS

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The purpose of any protective coating is to protect the base material from the environment which surrounds it. It follows, therefore, that the protective coating material must in itself have great resistance to the environment to which it is exposed. If the coating does not provide this protection then it has failed in its purpose.

Of necessity, cost is a factor in the selection of a protective coating. It is important, therefore, that the coating exhibit properties which when considered with the type of structure protected, the environment and the cost, will provide an economically sound system. Unfortunately, no one has yet developed a protective coating system which is reasonably priced and fully effective in all applications. Each exposure condition has its own unique characteristics which will take its toll of a coating system. Service testing, which implies testing under actual service conditions, will answer the question: How well is the coating system doing its job?

When considering a protective coating for application to a new facility, two things may be done. First, test panels coated with various systems under consideration may be exposed to environmental conditions considered to be typical of those to be encountered. Short term tests of this type provide valuable screening information and will generally eliminate from further consideration those protective coating systems which are totally unsuited for the job. Second, valuable information may be obtained from operating equipment where experience under actual service conditions may be available. The more complete the history of an existing coating system under operating conditions, the greater the value that can be placed on the conclusions drawn from this experience.

The basis for evaluating protective coatings rests heavily on the properties which the coatings exhibit. It would be well to review briefly some of the particular requirements and more important characteristic properties which coatings must have for exposure to general classes of environment.

In atmospheric service, a protective coating must have good adhesion or bond to the base material, resist actinic effects, rain, wind and dust, and must withstand a wide range of operating temperatures and the associated thermal shock. Also, the coating must be able to resist chemical attack from

the oxygen in the air and such compounds as may be present from a multitude of industrial sources as atmospheric contaminants.

Protective coatings when applied to process equipment may be subject to all the rigors of atmospheric exposure, plus additional specific conditions characteristic only of the process itself, or it may involve exposure to a very specific environment and set of operating conditions. In addition to good bond, the coating system must frequently resist abrasive effects and mechanical action. If the process involves a chemically specific environment, the coating must resist chemical attack and solvent action within economic limits and technical feasibility. In process equipment use of the protective coating may well be subject to extremely wide ranges of temperature.

In total and partial immersion service, such as wharf pilings, water tank interiors, dam gates and the like, a protective coating system is subject to a new set of environmental factors which will have a definite bearing on the serviceability of the coating system. It must have good bond to the base material, but also must have excellent mechanical strength to withstand floating debris, ice and other impact effects. Failure of the coating through cracks or chipping will frequently result in serious corrosion where the base metal is exposed. The coating material itself must be highly resistant to moisture absorption and it should be a non-conductor of electricity. For service where immersion in aqueous environments is involved the coating should be compatible with cathodic protection, i.e., it should resist highly alkaline conditions at the metal surface where cathodic currents enter protective coating faults. Finally, the physical properties should resist a relatively wide range of operating temperatures.

Coatings for service underground are subject to a wide range of variables. Excellent bond to the base material is essential since moisture penetration to the layers between the coating and the base metal can result in aggressive corrosion which may not be controllable with cathodic protection⁽¹⁾. Mechanically, the coating system must have excellent strength to resist soil movement and stress. As in the case of total immersion service, the coating should resist moisture absorption and have good electrical insulating properties even after long periods of exposure since galvanic currents and in some cases stray electric currents from manmade sources can be aggressively corrosive to the base metal if they pass

through the coating. The coating should be compatible with cathodic protection. For some kinds of service a chemical corrosion inhibitor may be included to assist in controlling local galvanic corrosion. Resistance to microbiological attack is a must since all soils contain many such organisms⁽²⁾⁽³⁾. Depending upon the specific application, the coating may have to resist a wide range of temperature effects although generally not so severe as atmospheric or process equipment conditions.

With these basic properties and the requirements in mind, it should be evident that service testing is about the only all inclusive way to evaluate the merits and limitations of protective coatings.

We have already noted that preliminary screening tests using panels or test coupons are most useful in eliminating totally ineffective materials from consideration on a specific application. Such tests generally require but a short time for completion and provide many practical advantages such as completeness of examination and accuracy of control. Unfortunately, such tests can not provide the complete story nor take into account all of the many variables associated with the final conditions to which the coating is to be subjected.

Service tests generally fall into two categories. The first is the direct tests which may be conducted where it is possible to physically examine the coating system under actual conditions of exposure. This would include coatings on structural members exposed to the atmosphere, on process equipment where it is possible during shut-down periods to directly examine the condition of the coating and, to a limited extent, on underground structures such as pipelines where it is possible to excavate the structure. The second type of test is that conducted using indirect methods to reach conclusions on coating effectiveness. Such tests are performed where it is not possible or economical to examine the coating by direct physical means.

It is not uncommon to set up comparative tests for evaluation of a number of different coating systems for a particular application. This will usually occur at a time when the original protective coating has shown signs of deterioration and it is evident that a complete recoating job will be required in the near future. Test areas selected to cover as many of the variables of exposure as possible are prepared and coated under the close supervision

of either the manufacturer or the plant engineer. The coatings selected for service tests are generally those which have, through experience, given the best service, or are the coatings which preliminary exposure tests have indicated should be most suitable for the specific job. The condition and changes in physical properties of the various coatings are then followed on a regular basis during the period of evaluation, and the final coating selected on the basis of the results.

In carrying out tests on protective coatings on equipment which is in service, it must be remembered that rigorously controlled conditions of the laboratory are not present, and it is most important that comparative data be obtained for all systems under test. It is also essential that excellent records be kept for future reference and comparison. Wherever possible inspection should be done on a statistical basis. This is particularly important in the case of extensive structures where considerable variations may occur from one point to another due to prevailing wind conditions, local environmental factors and temperature differences. It is for this reason that most in-service exposure tests for comparison of different coating systems will involve scattered test sites at quite a number of different locations rather than in one area.

The tests which may be performed on structures where direct access to the coating is possible are generally modifications of standard tests used in exposure testing. Appearance alone may represent a relatively significant comparative test where several coatings are involved; however, caution must be exercised to see that rust stains or other apparent areas of coating failure are truly the result of coating deterioration and are not merely rust stains originating from other areas.

Since bond to the base metal is a particularly important characteristic, some sort of bond or adhesion test should be employed when comparing protective coatings in service. A common test is to scribe two parallel lines $3/4$ -inch apart and 4 inches long through the protective coating to the base material. A square-ended putty knife of $3/4$ -inch width is then forced under the coating for approximately $1/2$ -inch. An attempt is then made to lift the coating from the surface without fracturing the coating film. If the coating pulls away from the base material this is indicative of relatively poor bond. Details of this type of test are described in the American Water Works Association Standard, C-203-62, Section 2.4⁽⁴⁾. On extremely heavy coatings and mastics, lack of bond may be detected by tapping areas of the coated surface

with the handle of a screwdriver or similar implement. Large areas of disbonded coating will have a distinct hollow sound to them. Puncturing of the coating at locations where such sounds are detected will clearly show the area of lack of bond. Blisters in a coating are another method of detecting lack of adhesion or bond between the coating and base material or between layers of the protective coating. For comparative purposes, it is desirable to record the relative size of such blisters and the number of blisters per unit area of inspection.

The presence of moisture at the metal surface is also evidence that bond is not adequate. Such moisture may be present even though no obvious path of entry can be found; this may be the result of penetration of moisture through coating pores with subsequent disbonding. Other evidence of poor bond may be undercutting, flaking or the lifting of a coating from the metal surface over appreciable areas.

If a particular type of service is subject to impact, the resistance of the coating to this type of action must be evaluated. Standard impact tests have been developed for certain specific applications on a controlled basis⁽⁴⁾. It is possible, however, to perform a modified impact test using a steel ball dropped from a specific height on a horizontal surface, or swung, pendulum fashion, against vertical surfaces. The weight of the ball and distance of drop will vary depending upon the specific coating under test. The principle behind such tests is that shock on the metal surface will disbond a protective coating a certain distance from the point of impact. By peeling away the disbonded coating around the impact point, a comparison among various coatings is possible using the area of disbonding as the index. Since temperature and other factors have a critical influence on this property, care must be taken to test the different coating systems under comparable conditions.

Pinholes in a protective coating may be found under some conditions by electrical inspection with a protective coating holiday detector. Care must be taken to see that surface moisture on the coating material is not responsible for indications of coating faults. Where there is doubt, a "patch" test may be employed to locate and evaluate this type of defect⁽⁵⁾. Fig. 1 shows diagrammatically how this test is performed. The coating is first covered with a thin slurry of kaolin or other iron-free clay; the purpose of which is to fill in pinholes and other holidays in the protective coating and provide an electrically conductive path which will retain

moisture. Over the kaolin is placed a layer of absorbent paper, such as paper towelling, followed by a water soaked layer of cotton flannel. A cathode consisting of an aluminum or copper plate is then held firmly against the area of test and a battery, capable of supplying 60 to 100 volts potential, is connected between the base metal and the metal cathode with the polarity as indicated. If coating holidays are present, a current will flow. Since the base metal is the anode, electrolysis will occur and metal ions will migrate into the absorbent paper. The presence of these ions may be detected with a chemical indicator such as potassium ferricyanide where steel is the base material. The number of pinholes can then be counted and recorded per unit area as an index of porosity. For heavy enamel coatings of the coal-tar and asphalt type, it is usual to apply direct current for a period of time which may be calculated in minutes by dividing 100 by the applied voltage.

Where direct examination of the coating is possible, tests may be performed on such things as moisture absorption by removing samples of the coating and subjecting them to laboratory tests. A common test for moisture in bituminous coatings is A. S. T. M. D95(6). Other effects which should be recorded when a direct examination is made are chalking, alligatoring, softening or embrittlement, color change or other evidence of decomposition of outer layers of the coating.

Where the coating is applied over iron or steel, it is possible to measure coating thickness with electronic instruments which are non-destructive and quite accurate. Variations in thickness are indications of cold flow and can be checked by this type of instrumentation. A thickness-time relationship can then be established over a period of inspections.

Other visual evidence of coating deterioration may be the presence of imbedded foreign material in the coating. This may be of particular concern on structures such as pipelines which have been exposed to underground conditions prior to examination.

Another test which may be indicative of coating quality, is an electrical conductance test. The specific application of this type of test to a coated pipeline is shown in Fig. 2. In general conductance is most important on structures which are normally immersed in an aqueous environment or which are buried in soil. It is, therefore, a test which requires considerably more preparation for inspection than most other tests where direct examination is involved.

As with the electrical "patch" test for coating faults, use is made of electrical instruments and techniques. Referring to Fig. 2, a section of the coating is selected for examination and the pipe is thoroughly cleaned with wet rags to remove adhering soil and foreign matter. As with the "patch" test, the surface is wiped with a slurry of kaolin to retain moisture and provide uniform contact between the coating surface and the cathode. A pad of wet cotton flannel or paper towelling is generally wrapped around the pipe between the coating and the cathode to assure a uniform electrical contact. The area of the test is controlled by the physical size of the pad. Two guard rings are employed on either side of the cathode to prevent electrical leakage current from reaching the cathode from the surrounding environment thus creating an error in the measurement. The coating conductance is calculated by dividing the current collected from the cathode by the voltage applied between the cathode and the pipe surface. Since the guard rings are outside the current measuring network, leakage current from the earth along the coating surface is eliminated. If an appreciable voltage drop occurs across the milliammeter, a correction must be made in the final calculation.

Exposure to an earth environment may result in degrading effects due to soil bacteria. This effect has been the subject of research in recent years and has been reported in many papers (1)(2)(3)(7). Removal of samples for laboratory evaluation appears to be the only practical test for bacterial attack on protective coatings.

To summarize the direct examination approach to service testing: Standard types of tests or their modification may be used for exposure evaluation of coating materials recognizing that the conditions of the tests are subject to many variables not present in a laboratory examination. A complete set of records of the conditions existing during the testing and the properties of the coating system as observed both initially and through all stages of the tests are a must. Tests of this type should be performed on a periodic basis so that a running record will be available. Photographs showing conditions described in the reports are extremely helpful in building a sound record which may be relied on for future reference.

Service testing of structures such as pipelines and other underground installations by indirect means is quite important to certain industries. The most useful tests which fall in this category are ones that can be performed at regular intervals so that a history of the coating system will evolve. Since great quantities of bituminous base protective

coatings are employed in pipeline work, much of the following discussion will relate to this type of structure. It should, however, be remembered that modifications of the techniques described may be employed for other types of exposure, such as pilings, bulkheading, underground storage tanks and similar structures.

While the majority of measurements employed for the indirect evaluation of protective coatings are electrical, one specific test involves a physical type of measurement. This is the evaluation of water-line friction coefficients by the Hazen and Williams formula. Mathematically, the formula for water flow is expressed as

$$v = 1.318 C r^{0.63} s^{0.54}$$

where: v = velocity in feet percent

r = the hydraulic radius in feet

s = the hydraulic slope in feet per foot

C = the Hazen and Williams coefficient

Comparisons obtained with various coating systems in pipelines are based on the "C" factor. A good "C" factor generally indicates an effective protective coating in a water main, failure of the coating will be reflected in deterioration of this factor with time. An interesting report covering results of this type of work with various lining and coating materials has been compiled by the New England Water Works Association⁽⁸⁾. Where fluids other than water are involved, various friction factor equations are available which are useful for evaluation purposes.

The underground pipeline lends itself particularly well to indirect measurement of exterior protective coating qualities. It is a relatively easy matter to locate major protective coating faults on such a system. This is done by the Pearson electronic holiday detector method illustrated in Fig. 3. An alternating current signal is applied between the pipeline under test and a relatively remote earth electrode or ground bed. The alternating current signal, usually about 1,000 cycles per second, uses the earth path in flowing from the ground bed to the structure. If there are protective coating faults present, the signal current will concentrate at these locations. This produces appreciable voltage gradients in the earth. These voltage gradients at the point of coating holidays are detected by an electronic amplifier connected to metal cleats worn by two people making the survey. Generally the spacing between the individuals in the survey party is about 50 feet. The tone produced

by the voltage gradient in the earth around the holiday is detected and reaches a maximum when one of the operators of the detecting equipment is directly over the coating fault while the other operator is 50 feet away over an area of sound coating. Using this method it is then possible to locate and then excavate the pipeline to determine the reason for the indicated unusual flow of current through the protective coating. Where damage or coating deterioration is not obvious, it may be desirable to perform the "patch" and electrical conductance tests already discussed.

It is also possible on a long pipeline to measure quite accurately the average coating conductance at various points along the line. In this way it is possible to evaluate several different coating systems on a single pipeline provided adequate test facilities are installed. The method consists of establishing millivolt test stations on the pipe which are used to measure the flow of current. Fig. 4 shows a typical arrangement of millivolt test stations used for this purpose. These test stations use the pipe as an electrical shunt to indicate current flow. They are calibrated by inserting a voltmeter, "E", between the two inner leads of the test station and applying a known direct current, "A", to the outer leads. A factor for the test station is then obtained by dividing the number of amperes used by the number of millivolts deflection. The factor is expressed in amperes per millivolt.

By installing such test stations at various points along the pipeline or between sections using different coating systems, it is possible to accurately measure differences in current at successive locations along the line. Thus, if a direct current "I" is applied between the pipeline and a relatively remote ground bed, the relative amounts of current picked up along the structure in different areas can be determined. With known quantities of current picked up within sections, it is necessary only to determine the average electrical driving force or voltage responsible for forcing the current from the earth through the coating to the pipe. This is done by measuring the voltage change " ΔV " produced between the pipe and an earth reference produced by current "I". Calculation of the average conductance for the section is obtained as indicated in Fig. 4. The results are expressed in mhos per square foot of coating. Details of this type of test are given in National Association of Corrosion Engineers Technical Committee Report T-3D(9).

An example of the value of coating conductance as a tool in evaluating protective coatings is given by the graph Fig. 5. This figure shows change in electrical conductance

with time on a section of coated pipeline in service and in this case represents an unusually rapid deterioration for one type of protective coating.

The graph in Fig. 6 shows the same kind of data plotted on semi-logarithmic paper; in this case the coating conductance in a rubble filled area is compared with that in other areas on the same pipeline. The data indicates that even after repair of coating faults in the rubble area, coating conductivity continues to rise at a higher rate than that in areas of normal fill. Long term data of this type is of great value to the corrosion engineer in selecting protective coatings for various applications in underground work.

As noted earlier, similar methods can be employed on structures other than long pipelines provided means are available for measuring the actual flow of current in and out of a given part of the structure in contact with the earth or aqueous environment.

Since the primary purpose of protective coatings is to control corrosion, one method of evaluation is to determine the rate of corrosion on a given structure coated according to a set of specifications. Polarization measurements are one approach to determining such rates of corrosion on buried structures. Methods are described in work done by the National Bureau of Standards⁽⁵⁾⁽¹⁰⁾ and by Dr. Milton Stern⁽¹¹⁾. The value of corrosion rate data in evaluating protective coating conditions rests in establishing a corrosion rate time relationship. Tests must be performed in an identical fashion at suitable intervals so that comparison is possible.

A modification of corrosion rate data for evaluation of coating condition would be the use of minimum current required for cathodic protection on a given system. Cathodic protection requires that a structure be polarized to a pre-determined level. The amount of current required to maintain this polarization over a period of time can be used as an index to the continued effectiveness of the coating. Increasing current requirements to maintain polarization is indicative of deterioration of the coating.

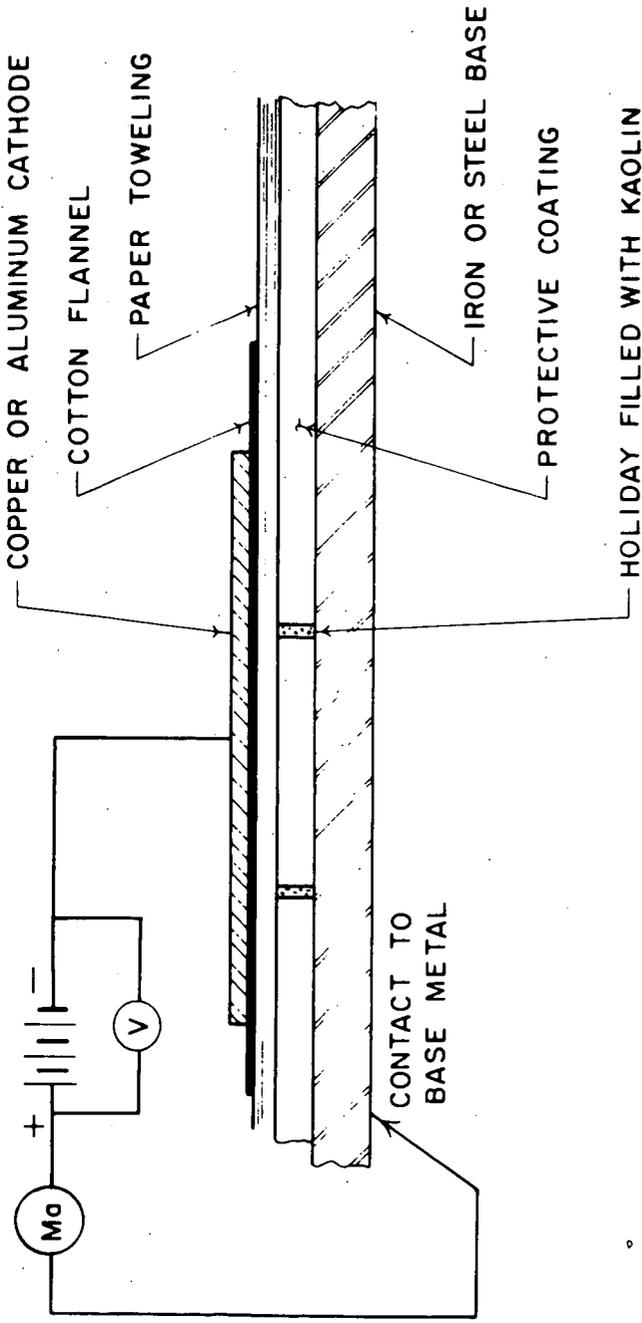
The electrical methods reviewed will indicate something about the effectiveness of the protective coating system; it will not, however, reveal what causes changes in characteristics. To obtain complete data requires some form of direct examination. Unfortunately, most of the tests described for indirect measurement are not of the type that can be readily

formulated into standard procedures. There are entirely too many variables associated with the types of structures involved and local conditions which may significantly affect the accuracy of the tests; a great deal of reliance must be placed on the experience of the engineer in carrying out the tests and in his ability to interpret the results.

Perhaps in time, improvements on techniques and other methods of testing will be developed so that specific problems of indirect in-service testing of coatings will be possible with results that can be compared to the direct access methods.

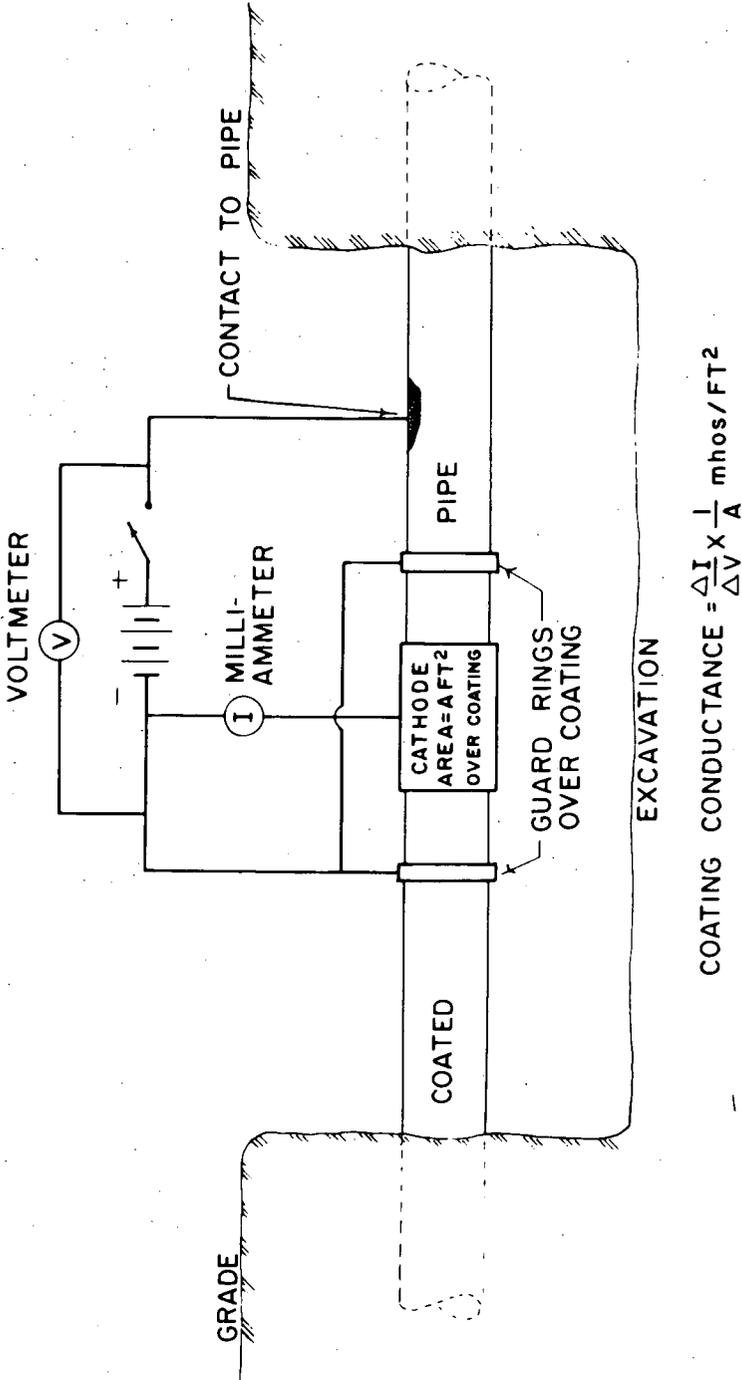
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- (11) Stern, Milton, "A Method for Determining Corrosion Rates from Linear Polarization Data". "Corrosion" Vol. 14, 1958, pp 440t - 444t.



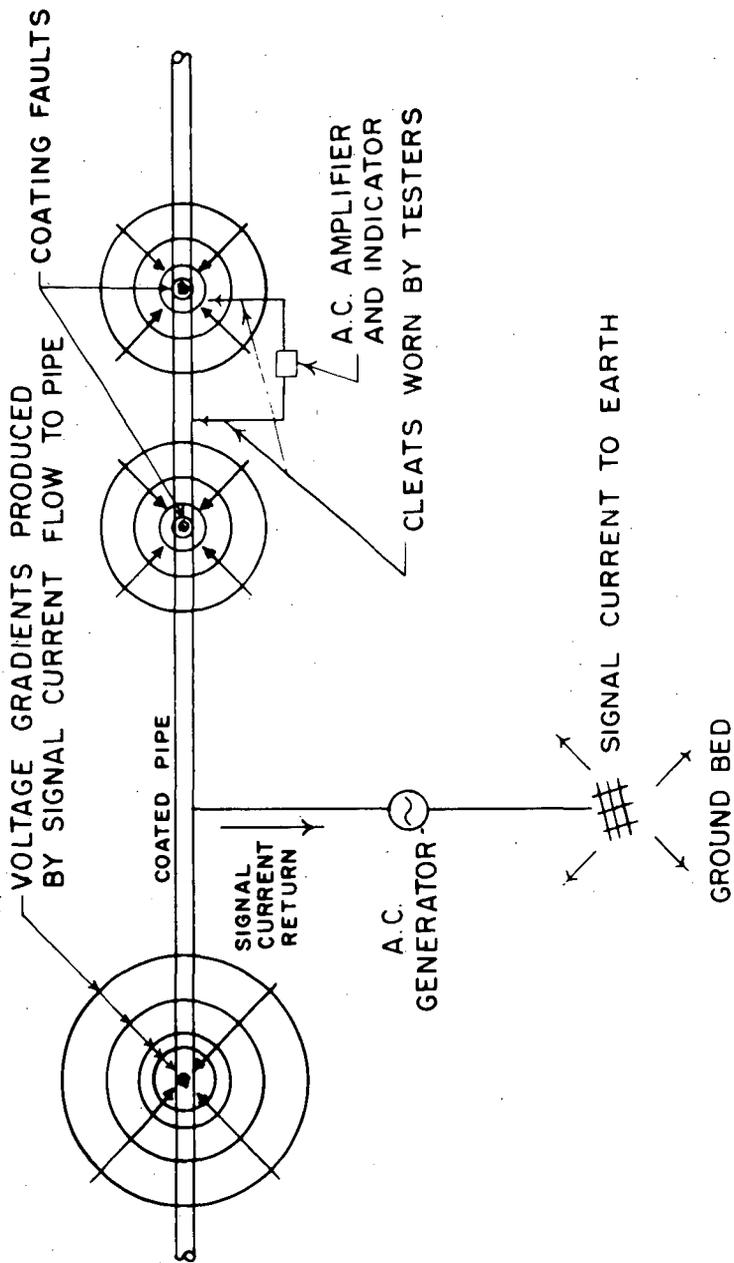
PATCH TEST FOR COATING FAULTS

FIGURE 1



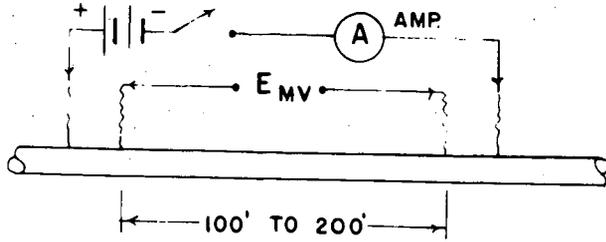
CONDUCTANCE MEASUREMENTS

FIGURE 2



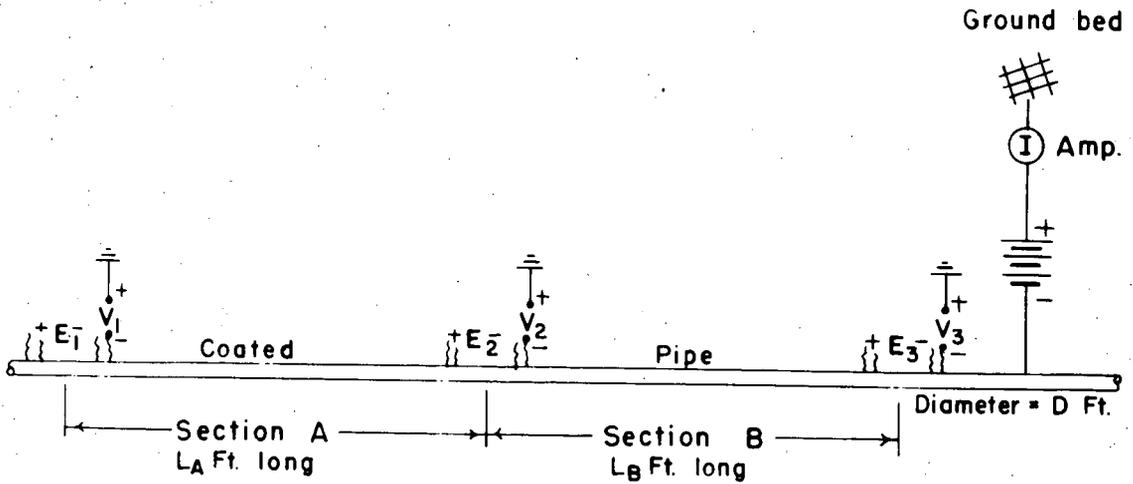
PEARSON COATING FAULT DETECTOR

FIGURE 3



$$\text{Factor} = \frac{\Delta A}{\Delta E} \text{ AMPS/M.V.} = K$$

CALIBRATION SET UP



$$\begin{aligned} \text{Average Conductance, Section A} &= \frac{\Delta E_2 \times K_2 - \Delta E_1 \times K_1}{\Delta I} \times \frac{2 \Delta I}{\Delta V_1 + \Delta V_2} \times \frac{1}{\pi \times D \times L_A} \\ &= \frac{\text{mhos}}{\text{FT}^2} \end{aligned}$$

FIGURE 4

FIGURE 5

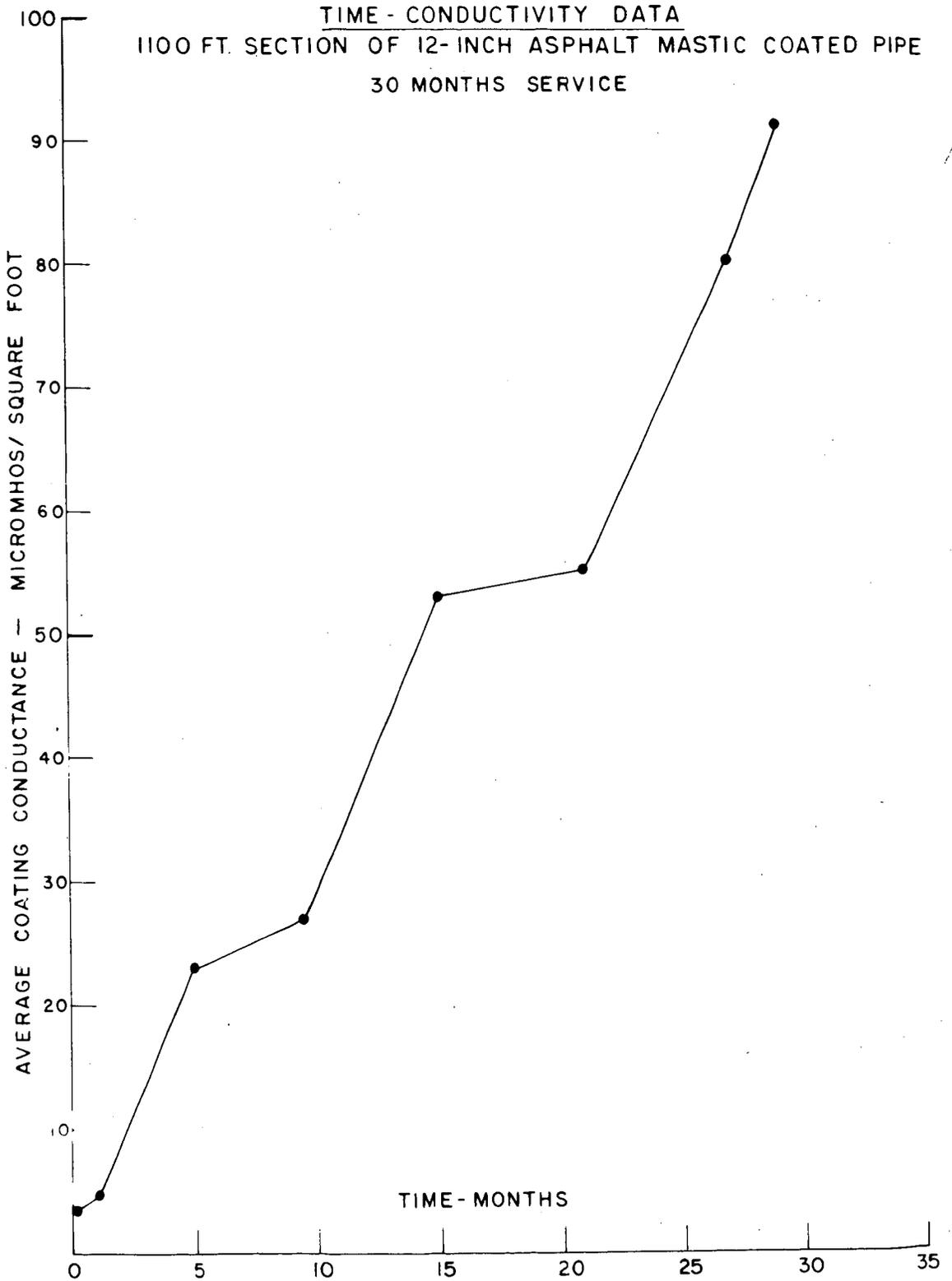
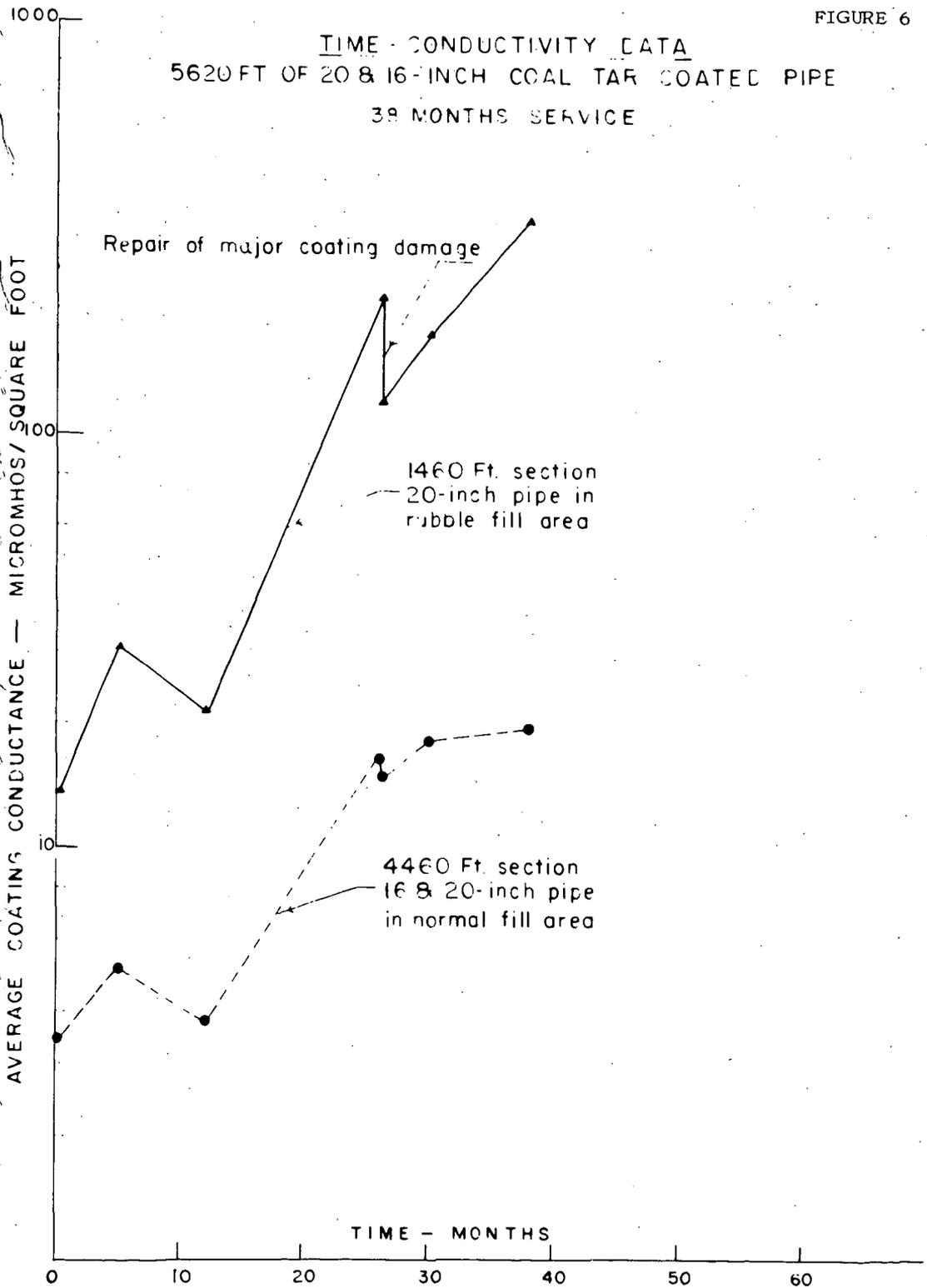


FIGURE 6

TIME - CONDUCTIVITY DATA
5620 FT OF 20 & 16-INCH COAL TAR COATED PIPE
39 MONTHS SERVICE



BITUMEN ATTACK BY MICROORGANISMS

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IT IS GENERALLY RECOGNIZED TODAY THAT A VARIETY OF BITUMINOUS MATERIALS ARE SUBJECT TO ATTACK BY MICROORGANISMS (1,2,3). EARLY REPORTS FROM OUR LABORATORY CONFIRM THE FACT THAT ASPHALTS ARE DEGRADED BY A VARIETY OF BACTERIA (4,5). THE PURPOSE OF THIS PAPER IS TO SUMMARIZE THE EXTENT OF OUR RESEARCH INTO THE ATTACK OF BITUMINOUS MATERIALS BY MICROORGANISMS. MOST OF OUR STUDIES DEAL WITH BITUMINOUS MATERIALS OF PETROLEUM ORIGIN AND WILL EMPHASIZE: (A) THE NATURE OF THE ORGANISMS ATTACKING BITUMENS (B) THE NATURE OF THE MICROBIAL ACTION ON BITUMEN AND (C) THE ASPHALTIC CONSTITUENTS UTILIZED BY BACTERIA.

ASPHALT UTILIZING ORGANISMS

A TYPICAL PAVING ASPHALT (135 PENETRATION) DESIGNATED AS "1A" WAS USED FOR ENRICHMENT CULTURE ISOLATION OF BACTERIA CAPABLE OF UTILIZING BITUMEN. THE ORGANISMS OBTAINED WERE SHOWN TO BE MEMBERS OF THE GENERA Pseudomonas, Achromobacter, Micrococcus, Flavobacterium, Bacillus, Corynebacterium AND Alcaligenes. LATER IT WAS SHOWN THAT CERTAIN ORGANISMS IN THE GENERA Mycobacterium AND Nocardia GREW WELL ON ASPHALT SUBSTRATES. THESE RESULTS DEMONSTRATE THE DIVERSITY OF MICROORGANISMS CAPABLE OF UTILIZING A BITUMEN OF THIS NATURE.

A SOIL BURIAL TEST WAS DEvised USING A VARIETY OF BITUMENS COATED ON BIRCH TONGUE BLADES AND EXPOSED IN SOIL UNDER NATURAL CONDITIONS. ONE SET OF BLADES WAS BURIED IN A SOIL WITH A HIGH MOISTURE CONTENT (16%) AND A DUPLICATE SET IN A SIMILAR SOIL BUT UNDER LOW MOISTURE (6.4%) CONDITIONS. ACTION WAS SCORED BY DETERMINING THE WEIGHT LOSS OF THE BITUMEN COAT FROM

THE TONGUE BLADES AT VARYING TIME INTERVALS. THE RESULT OF ONE SERIES OF EXPERIMENTS IS SHOWN IN FIG. 1.

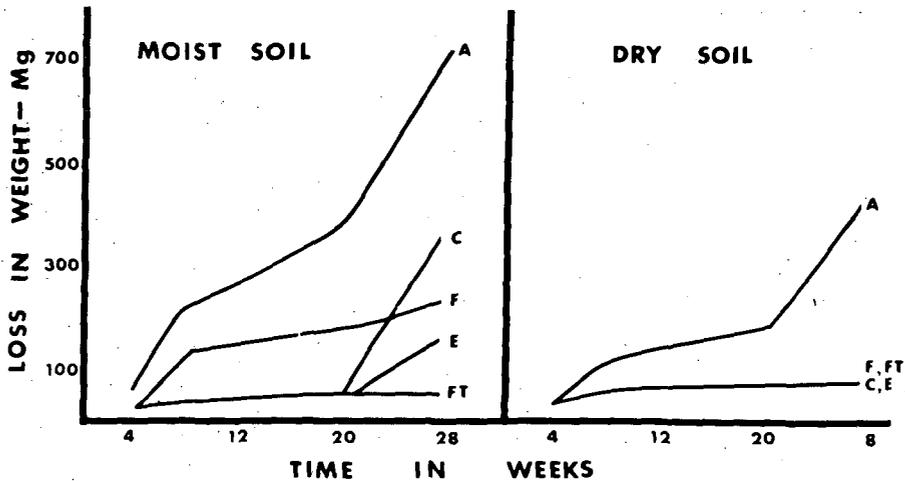


FIG. 1:--EFFECT OF SOIL BURIAL ON WEIGHT LOSS OF BITUMEN COATED TONGUE BLADES.

BITUMEN "A" IS MOST SUSCEPTIBLE TO WEIGHT LOSS IN MOIST SOIL, FOLLOWED IN ORDER BY BITUMENS "C," "F," AND "E." BITUMEN "FT" WAS REPORTED TO BE TREATED WITH A BACTERICIDAL MATERIAL AND DOES NOT SHOW A WEIGHT LOSS EVEN AFTER 28 WEEKS OF EXPOSURE IN MOIST SOIL. IN DRY SOIL APPARENTLY ALL OF THE BITUMENS EXCEPT "A" ARE RESISTANT TO WEIGHT LOSS. IT WOULD APPEAR THAT MOISTURE LEVEL IS INDEED CRITICAL (6) AS POINTED OUT BY HARRIS. ALSO, IT IS OBVIOUS THAT THE BITUMENS DIFFER IN THEIR SUSCEPTIBILITY TO SOIL EFFECTS.

THE DIFFERENCE IN SUSCEPTIBILITY OF BITUMEN TO BACTERIAL ACTION IS FURTHER SUPPORTED BY LABORATORY EXPERIMENTS (5). IT WAS DEMONSTRATED THAT Bacillus 11-2A ISOLATED BY ENRICHMENT CULTURE WOULD READILY ATTACK ASPHALT 6A, AND UTILIZE BITUMENS "A" AND "E" TO A LESSER EXTENT, BUT WAS UNABLE TO UTILIZE ASPHALT "G." ALL OF THESE MATERIALS WERE DEMONSTRATED TO SERVE AS A GROWTH SUBSTRATE FOR A Flavobacterium. THIS IS FURTHER EVIDENCE FOR THE SPECIFICITY OF ACTION OF A BACTERIUM ON DIFFERENT BITUMENS. SOME OF THE CHARACTERISTICS OF THESE MATERIALS ARE PRESENTED IN TABLE I, FROM WHICH IT IS SEEN THAT THESE MATERIALS VARY IN THEIR PHYSICAL NATURE. IT IS LOGICAL TO CONCLUDE THAT THE MICROBIAL ATTACK ON BITUMENS IS SPECIFIC. THE SPECIFICITY IS DETERMINED NOT ONLY BY THE NATURE OF THE BACTERIUM BUT ALSO BY THE CHEMICAL COMPOSITION OF THE BITUMEN.

TABLE I

PROPERTIES OF BITUMENS USED IN SOIL BURIAL TESTS AND GROWTH STUDIES.

BITUMEN	SOFTENING POINT	SPECIFIC GRAVITY	PENETRATION
	°F	77°F	77°F/100F/5 SEC MM/10
6A	111	0.985	133
A	195	1.015	48
E	167	1.175	0
G	161	1.269	0
C	214	1.06	3
F	170	1.195	0
FT	173	1.226	0

NATURE OF ACTION

THE RATE OF BITUMEN DETERIORATION UNDER NATURAL CONDITIONS CAN VARY TO A LARGE EXTENT DEPENDING UPON THE MATERIAL AND THE CONDITIONS OF EXPOSURE. IT IS NOT THE PURPOSE OF THIS PAPER TO DWELL UPON THE CONDITIONS OF EXPOSURE. THE WEIGHT LOSS EXPERIMENTS SHOWN IN FIG. 1 MIGHT BE CONSIDERED AN INDEX OF SUSCEPTIBILITY TO THE MICROBIAL POPULATIONS IN THE SOIL. IT IS DOUBTFUL IF THE WEIGHT LOSS IN THESE EXPERIMENTS IS DUE ENTIRELY TO MICROBIAL ACTION. NATURAL WEATHERING EFFECTS PLUS SOIL ABSORPTION COULD ALSO BE INVOLVED IN THIS WEIGHT LOSS. HOWEVER, IT IS LIKELY THAT MICROBIAL ACTION ACCOUNTS FOR THE MAJOR PORTION OF THE LOSS. EARLIER REPORTS (4,5) CITE DEGRADATIVE ACTIVITY OF A NUMBER OF PURE CULTURES ON A SINGLE ASPHALT UNDER LABORATORY CONDITIONS. IN THESE EXPERIMENTS THE RATE OF BREAKDOWN WAS RAPID, 3% TO 25% DEGRADATION OCCURRING WITHIN ONE WEEK OF EXPOSURE UNDER OPTIMUM CONDITIONS OF TEMPERATURE, pH AND AERATION. THERE IS A VAST DIFFERENCE BETWEEN THE LABORATORY CONDITIONS AND THE SOIL BURIAL TEST, IN THAT EXTREMELY THIN FILMS OF ASPHALT WERE USED IN THESE LABORATORY EXPERIMENTS AND RELATIVELY THICK FILMS IN THE SOIL BURIAL EXPERIMENTS. IT IS APPARENT FROM EARLY EXPERIMENTS THAT THE BACTERIAL ATTACK IS ONLY AT THE SURFACE OF THE BITUMEN. WITH THE THIN FILM MOST OF THE BITUMEN IS EXPOSED AS A SURFACE AND THEREFORE AVAILABLE TO THE ORGANISM. IN THE SOIL BURIAL TESTS AND IN-USE THE BITUMEN IS APPLIED AS A RELATIVELY THICK FILM; THEREFORE, ONLY A SMALL OVER-ALL PORTION OF THE BITUMEN IS EXPOSED TO MICROBIAL ACTION.

THE THIN FILM PROVIDES VISUAL EVIDENCE FOR THE MICROBIAL ACTION. FIG. 2 SHOWS A FLASK ON THE LEFT CONTAINING A FILM OF ASPHALT 1A INOCULATED WITH Mycobacterium ranae AND ON THE RIGHT AN IDENTICAL FLASK WITHOUT THE TEST ORGANISM. AFTER INCUBATION



FIG. 2:--EFFECT OF *Mycobacterium ranae* ON ASPHALT 1A FILM. TEST FLASK ON LEFT, CONTROL FLASK ON RIGHT. INCUBATION 30°C FOR 1 MONTH.

AT 30°C FOR 1 MONTH THE FILM IN THE TEST FLASK HAS BROKEN AND SETTLED TO THE BOTTOM, WHEREAS THE CONTROL FILM IS UNCHANGED. EVEN MORE SIGNIFICANT IS THE APPEARANCE OF ASPHALT SAMPLES FROM EACH FLASK (FIG. 3). THE TEST ASPHALT IS DULL, ROUGH, CRUMBLY AND HAS LOST ITS USUAL RHEOLOGICAL CHARACTERISTICS, WHEREAS THE SAMPLE FROM THE CONTROL FLASK IS NOT CHANGED IN ITS CHARACTERISTICS.

HARRIS ET AL. (7) PERFORMED A SERIES OF EXPERIMENTS TO DETERMINE THE EFFECT OF VARIOUS BACTERIA ON PAVING ASPHALTS. THEY USED SOFTENING POINT, DUCTIBILITY AND PENETRATION MEASUREMENTS TO DETERMINE THE ACTION OF THE ORGANISMS AND CONCLUDED THAT EITHER A SOFTENING OR HARDENING OF THE ASPHALTS OCCURRED, DEPENDING ON THE NATURE OF THE BACTERIA PRESENT. IN ORDER TO

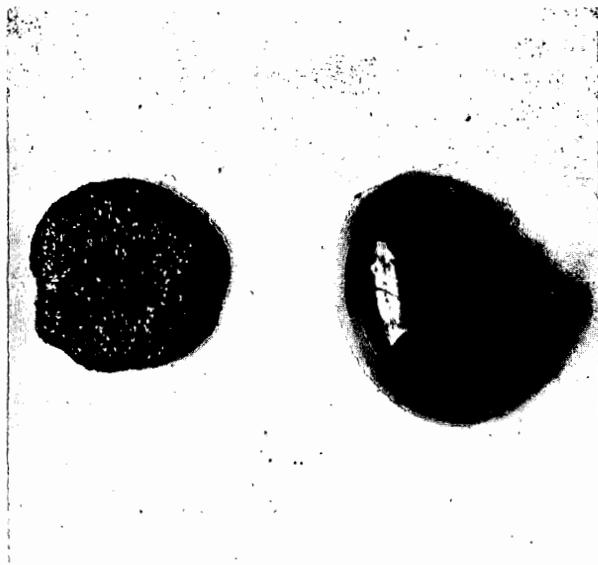


FIG. 3:--ASPHALT SAMPLES COLLECTED FROM CULTURE FLASKS. TEST FLASK ON LEFT, CONTROL FLASK ON RIGHT.

ACCURATELY ASSESS THE EFFECT OF THE ORGANISMS WE MUST ATTEMPT TO EXPOSE THE MAJOR PORTION OF THE ASPHALT TO MICROBIAL ACTION. AN EMULSION SYSTEM WAS USED AND THE ASPHALTS EXPOSED TO Mycobacterium ranae AND Nocardia coeliaca AT 30°C FOR 4 MONTHS. THE ASPHALTS WERE RECOVERED AND EXAMINED FOR CHANGES IN VISCOSITY. STERILE CONTROLS WERE TREATED IN THE SAME MANNER AS THE TEST FLASKS AND USED TO DETERMINE RELATIVE VISCOSITY OF ASPHALT DEGRADED BY THE MICROORGANISMS. TABLE II SHOWS THAT THE NET EFFECT OF THESE TWO ORGANISMS WAS TO INCREASE THE VISCOSITY OF THE THREE ASPHALTS TESTED. IT IS SIGNIFICANT THAT THE THREE ASPHALTS INVESTIGATED VARY CONSIDERABLY IN THEIR SUSCEPTIBILITY TO MICROBIAL ACTION (AS EVIDENCED BY THE VISCOSITY DATA). IT IS LOGICAL TO ASSUME THAT THIS EFFECT IS

TABLE II

RELATIVE VISCOSITY OF ASPHALTS AFTER MICROBIAL ACTION.

<u>ASPHALT</u>	<u>RELATIVE VISCOSITY*</u>	
	<u>M. ranae</u>	<u>N. coeliaca</u>
1A	2.0	1.4
3A	3.3	3.8
6A	-	6.8

*RELATIVE VISCOSITY = $\frac{\text{VISCOSITY DEGRADED ASPHALT}}{\text{VISCOSITY CONTROL ASPHALT}}$

CONTROL ASPHALTS NOT EXPOSED TO MICROBIAL ACTION. VISCOSITY CALCULATED AT 5×10^{-2} SEC⁻¹ RATE OF SHEAR WERE APPROXIMATELY 500,000 POISES AT 25°C.

TIED IN WITH THE ACTION OF THE ORGANISMS ON SOME ASPHALT COMPONENT THAT IS SUSCEPTIBLE TO MICROBIAL ACTION AND IS ALSO RELATED TO THE RHEOLOGICAL CHARACTERISTICS OF THESE ASPHALTS.

THE RELATION BETWEEN ASPHALT COMPOSITION AND HARDENING IS NOT WELL DEFINED BUT SOME INFORMATION IS NOW AVAILABLE (8). CONSIDERABLE EVIDENCE HAS ACCUMULATED OVER THE YEARS WHICH SHOWS THAT ASPHALTS HARDEN WITH AGING AND WHEN SUBJECTED TO HEAT, OXYGEN, OR ACTINIC LIGHT. THIS HARDENING REDUCES THE ADHESIVENESS AND THEREFORE THE IN-SERVICE DURABILITY OF THE MATERIAL. THESE HARDENING EFFECTS CAN TO A LARGE EXTENT BE DUE TO OXIDATION OF CERTAIN ASPHALT COMPONENTS. THE EFFECT OF MICROBIAL ACTION ON THE ASPHALT WOULD BE EXPECTED TO INVOLVE PRIMARILY OXIDATION OF THOSE ASPHALT COMPONENTS UTILIZED FOR GROWTH BY THE MICROORGANISM.

TABLE III

GROWTH OF TEST ORGANISMS ON ASPHALT AND ASPHALT FRACTIONS.

ASSAY MATERIAL	<u>Ps. 196Aa</u>	<u>M. ranae</u>	<u>N. coeliaca</u>
ASPHALT 1A	-	+	+
ASPHALTENES 1A	-	+	+
ACETONE ELUATE 1A	-	+	+
BASE MATERIAL 1A	+	+	::
ASPHALT 3A	-	+	+
ASPHALTENES 3A	-	+	+
ACETONE ELUATE 3A	-	+	-
BASE MATERIAL 3A	+	+	::
ASPHALT 6A	-	+	+
ACETONE ELUATE 6A	-	+	-
BASE MATERIAL 6A	+	+	::

::NOT TESTED

TABLE III SUMMARIZES SOME PRELIMINARY DATA FROM STUDIES IN OUR LABORATORY ON THOSE FRACTIONS FROM THREE ASPHALTS UTILIZED FOR GROWTH BY SELECTED MICROORGANISMS. Pseudomonas 196Aa UTILIZES ONLY THE BASE MATERIAL FROM THE THREE ASPHALTS AND WILL NOT GROW ON THE UNFRACTIONATED ASPHALT. Mycobacterium ranae, WHICH WAS SHOWN TO DRASTICALLY MODIFY THE ASPHALT (VISCOSITY STUDIES), IS ABLE TO UTILIZE ALL FRACTIONS WHICH HAVE BEEN STUDIED. Nocardia coeliaca, WHICH ALSO HAS A DRASTIC EFFECT ON VISCOSITY, WILL UTILIZE ALL FRACTIONS TESTED EXCEPT THE ACETONE ELUATE. THE BASE MATERIAL HAS A CONSIDERABLE ALIPHATIC HYDROCARBON CONTENT, AS WILL BE POINTED OUT LATER. Nocardia coeliaca IS KNOWN TO GROW ON MANY OF THE n-ALKANES; THEREFORE IT WILL LIKELY UTILIZE THE BASE MATERIAL.

IN ORDER TO SIMPLIFY THE APPROACH TO THIS PROBLEM THE ASPHALTS WERE FRACTIONATED INTO NARROW FRACTIONS OF SOMEWHAT SIMILAR COMPOUNDS. THE ASPHALTENES (PENTANE INSOLUBLE) WERE SEPARATED FROM THE PETROLENES (PENTANE SOLUBLE) BY TREATMENT WITH N-PENTANE. THE PENTANE SOLUBLE PETROLENES WERE EXTRACTED WITH SULFURIC ACID FOLLOWED BY CHROMATOGRAPHIC FRACTIONATION ON A FLORISIL COLUMN. THE n-PENTANE ELUATE FROM THE FLORISIL COLUMN (BASE MATERIAL) WAS FURTHER FRACTIONATED BY THERMAL DIFFUSION TO PROVIDE NARROW FRACTIONATION OF THE LOWER MOLECULAR WEIGHT AND LESS POLAR PORTIONS OF THE ASPHALTS. ACETONE WAS USED TO FURTHER STRIP THE FLORISIL COLUMN AND REPRESENTS THE ACETONE ELUATE (TABLE III).

THE BASE MATERIAL AND 10 THERMAL DIFFUSION FRACTIONS HAVE RECEIVED THE MOST EXTENSIVE STUDY TO DATE. INFRARED SPECTROPHOTOMETRIC ANALYSIS AND MICROBIAL GROWTH STUDIES HAVE BEEN PERFORMED ON THESE FRACTIONS.

FIGS. 4, 5 AND 6 SHOW THE INFRARED SPECTRA OF THE BASE MATERIAL AND 10 THERMAL DIFFUSION FRACTIONS FROM EACH OF THE THREE ASPHALTS STUDIED (1A, 3A AND 6A). IT SHOULD BE POINTED OUT THAT FRACTION 1 IS FROM THE BOTTOM OF THE COLUMN AND FRACTION 10 FROM THE TOP. ALL BAND POSITIONS ARE REPORTED IN RECIPROCAL CENTIMETERS (CM^{-1}) AND EXPRESSED AS PEAK HEIGHTS RELATIVE TO THOSE INTENSITIES OF FRACTION 1. THE FRACTIONS FROM ASPHALT 1A HAVE CONSIDERABLY MORE ALIPHATIC CHARACTER THAN THOSE FROM THE OTHER TWO ASPHALTS. THERE IS CONSIDERABLE AROMATICITY PRESENT IN THE 1A AND 3A ASPHALT FRACTIONS. IT IS APPARENT EXCEPT FOR FRACTION 10 OF ASPHALT 1A, 3A AND 6A WHICH ARE PREDOMINATELY ALIPHATIC ALL THESE FRACTIONS ARE A MIXTURE OF ALIPHATIC AND AROMATIC COMPOUNDS.

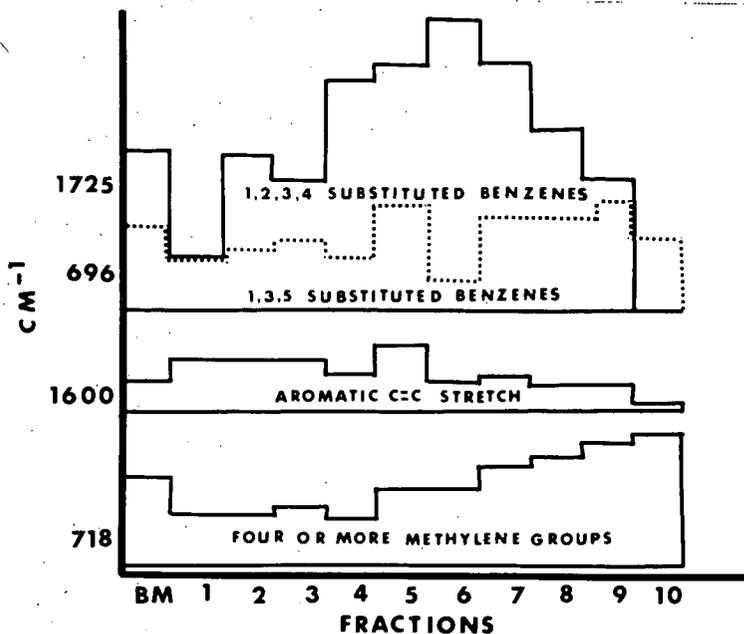
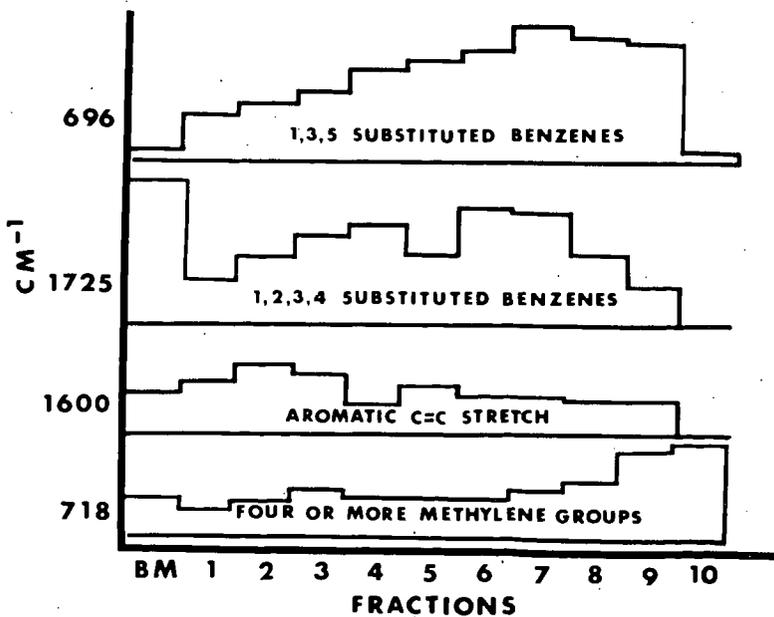


FIG. 4:--

INFRARED SPECTRA
OF BASE MATERIAL
AND THERMAL
DIFFUSION FRACTIONS
FROM ASPHALT 1A.

FIG. 5:--

INFRARED SPECTRA OF
BASE MATERIAL AND
THERMAL DIFFUSION
FRACTIONS FROM
ASPHALT 3A.



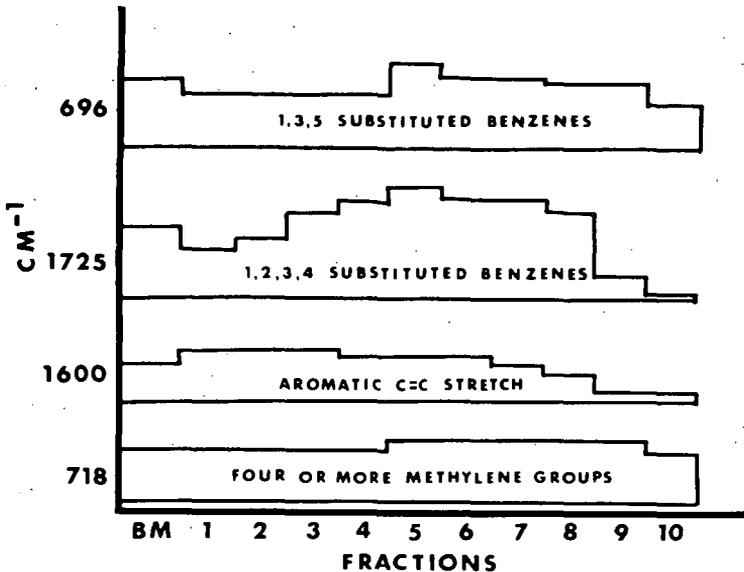


FIG. 6:--INFRARED SPECTRA OF BASE MATERIAL AND THERMAL DIFFUSION FRACTIONS FROM ASPHALT 6A.

EACH FRACTION WAS ASSAYED FOR GROWTH SUPPORTING ACTIVITY WITH Mycobacterium ranae AND Pseudomonas 196Aa. TABLE IV SHOWS THE MAXIMUM TURBIDITY DEVELOPING ON EACH FRACTION IN THE Pseudomonas 196Aa ASSAYS. Pseudomonas WILL GROW ONLY ON THE TOP FRACTIONS WHICH ARE DEMONSTRATED TO BE ALIPHATIC IN NATURE. THE INFRARED DATA, HOWEVER, DEMONSTRATES THE PRESENCE OF ALIPHATIC MATERIALS IN ALL THERMAL DIFFUSION FRACTIONS.

THE HYDROCARBON SPECIFICITY DATA (TABLE V) DEMONSTRATES THAT Pseudomonas 196Aa IS LIMITED TO THE UTILIZATION OF n-ALKANES (C-6 TO C-22), ALKENES (C-8, C-10, C-12 AND C-14) AS WELL AS CERTAIN OF THE FATTY ACIDS. THIS ORGANISM WAS INCAPABLE OF

TABLE IV

GROWTH OF Pseudomonas 196Aa ON THERMAL DIFFUSION FRACTIONS.

FRACTION SOURCE	MAXIMUM TURBIDITY										
	BM ²	1	2	3	4	5	6	7	8	9	10
ASPHALT 1A	64	0	0	0	0	0	0	0	0	25	116
ASPHALT 3A	35	0	0	0	0	0	0	0	0	58	175
ASPHALT 6A	32	0	0	0	0	0	0	0	0	0	122

RESULTS IN KLETT UNITS AFTER 72 HRS. INCUBATION AT 32°C.

*BASE MATERIAL

TABLE V

SUBSTRATE SPECIFICITY OF Pseudomonas 196Aa.

n-ALKANES

LEXANE	175
LEPTANE	195
OCTANE	200
NONANE	229
DECANE	200
DODECANE	220
TRIDECANE	230
TETRADECANE	260
HEXADECANE	260
OCTADECANE	200
EICOSANE	250
DOCOSANE	220

ALKENES

1-HEPTENE	0
1-OCTENE	210
1-DECENE	178
1-DODECENE	120
1-TETRADECENE	300
1-HEXADECENE	0

FATTY ACIDS

LEXANOIC	75
LEPTANOIC	105
OCTANOIC	115
NONANOIC	100
DECANOIC	95
DODECANOIC	183
-	
TETRADECANOIC	180
HEXADECANOIC	190
OCTADECANOIC	260
-	
BEHENIC	0

AROMATIC

BENZENE	0
ETHYLBENZENE	0
PROPYLBENZENE	0
TRIMETHYLBENZENE	0
PENTAMETHYLBENZENE	0
HEXAMETHYLBENZENE	0
XYLENES (O,M,P)	0
TOLUENE	0

GROWTH ON ANY OF THE AROMATIC HYDROCARBONS TESTED. THE DECREASED GROWTH RESPONSE OF Pseudomonas 196Aa ON THE BASE MATERIALS FROM THE THREE ASPHALTS AND FRACTION 9 FROM ASPHALTS 1A AND 3A, AS WELL AS THE COMPLETE ABSENCE OF GROWTH ON FRACTION 9 OF ASPHALT 6A, IS DIFFICULT TO UNDERSTAND IF THE ORGANISM IS CAPABLE OF UTILIZING THE ALKANE SHOWN BY INFRARED ANALYSES TO BE PRESENT IN THESE MATERIALS (FIGS. 4, 5 AND 6). IT IS APPARENT THAT THE RATIO OF AROMATIC MATERIAL TO ALIPHATIC MATERIAL IS GREATER IN THOSE FRACTIONS NOT SUPPORTING THE GROWTH OF Pseudomonas 196Aa THAN THE FEW FRACTIONS WHICH DO SUPPORT GROWTH OF THIS ORGANISM. IT WOULD APPEAR, THEREFORE, THAT Pseudomonas 196Aa CAN UTILIZE THE n-ALKANES (OR ALKANE DERIVATIVES) PRESENT IN THE ASPHALT FRACTIONS, BUT THE ORGANISM IS INHIBITED IN THE PRESENCE OF SUBSTITUTED BENZENE COMPOUNDS.

THE RESULTS OF THE EXPERIMENT SHOWN IN TABLE VI CONFIRM THE INHIBITION OF n-ALKANE OXIDATION BY Pseudomonas 196Aa IN THE PRESENCE OF AROMATIC HYDROCARBONS. THE GREATER THE AROMATICITY OF THE COMPOUND, THE GREATER THE INHIBITION OF n-OCTANE UTILIZATION. BENZENE WAS SHOWN TO BE THE MOST INHIBITORY COMPOUND FOLLOWED BY TOLUENE, PROPYLBENZENE AND FINALLY TRIMETHYLBENZENE, WHICH IS NOT INHIBITORY. TRIMETHYLBENZENE APPARENTLY IS UTILIZED IN THE PRESENCE OF n-OCTANE, BUT NOT ALONE. THIS EFFECT HAS NOT BEEN FULLY INVESTIGATED AT THIS TIME BUT MAY REPRESENT A CO-OXIDATION EFFECT (9).

THE GROWTH RESPONSE PATTERN OF Mycobacterium ranae ON THE THERMAL DIFFUSION FRACTIONS (TABLE VII) IS COMPLETELY DIFFERENT FROM THE Pseudomonas PATTERN. THIS ORGANISM IS CAPABLE OF GROWTH ON ALL OF THE ASPHALT 6A FRACTIONS, AND MOST OF THE 3A AND 1A FRACTIONS. IT WOULD APPEAR THAT Mycobacterium ranae IS NOT AS SELECTIVE AS Pseudomonas 196Aa IN THE MATERIALS THAT IT CAN UTILIZE.

TABLE VI

EFFECT OF AROMATIC HYDROCARBONS ON n-OCTANE UTILIZATION BY Pseudomonas 196Aa.

AROMATIC HYDROCARBON	TURBIDITY IN KLETT UNITS	
	18 HRS.	20 HRS.
CONTROL	55	115
0.2% BENZENE	40	60
1.0% BENZENE	0	0
0.2% TOLUENE	115	160
0.2% PROPYL BENZENE	110	170
1.0% PROPYL BENZENE	5	15
2.0% PROPYL BENZENE	0	0
1.0% TOLUENE	0	0
0.2% TRIMETHYLBENZENE	180	200
1.0% TRIMETHYLBENZENE	115	140
2.0% TRIMETHYLBENZENE	90	115

2% n-OCTANE IN ALL FLASKS

TABLE VII

GROWTH OF Mycobacterium ranae ON THERMAL DIFFUSION FRACTIONS.

FRACTION SOURCE	BM*	MAXIMUM TURBIDITY									
		1	2	3	4	5	6	7	8	9	10
ASPHALT 1A	70	0	0	18	95	97	136	154	117	33	0
ASPHALT 3A	182	58	82	85	131	164	185	203	49	0	0
ASPHALT 6A	202	26	48	143	68	87	72	155	128	52	200

RESULTS IN KLETT UNITS AFTER 72 HRS. INCUBATION AT 32°C.

*BASE MATERIAL

EXAMINATION OF THE SPECIFICITY DATA OF THIS ORGANISM FOR PURE HYDROCARBONS (TABLE VIII) INDICATES IT IS NOT ONLY ABLE TO UTILIZE n-ALKANES (C-12 TO C-22) BUT ALSO SOME ALKENES, FATTY ACIDS AND ALL OF THE AROMATIC HYDROCARBON TESTED EXCEPT BENZENE.

<u>TABLE VIII</u>			
SUBSTRATE SPECIFICITY OF <u>Mycobacterium ranae</u> .			
<u>n-ALKANES</u>		<u>FATTY ACIDS</u>	
HEPTANE	0	HEPTANOIC	5
OCTANE	0	OCTANOIC	5
DECANE	0	DECANOIC	5
DUDECANE	55	DUDECANOIC	80
TRIDECANE	60	-	
TETRADECANE	60	TETRADECANOIC	125
HEXADECANE	60	HEXADECANOIC	65
OCTADECANE	60	OCTADECANOIC	170
EICOSANE	125	-	
DOCOSANE	75	BEHENIC	40
<u>ALKENES</u>		<u>AROMATIC</u>	
1-DODECENE	0	BENZENE	0
1-TETRADECENE	40	ETHYLBENZENE	95
1-HEXADECENE	85	PROPYLBENZENE	58
1-OCTADECENE	75	TRIMETHYLBENZENE	112
1-NONADECENE	75	XYLENES (O,M,P)	126-163
		TOLUENE	99

IT IS CONCLUDED FROM THIS DATA THAT Mycobacterium ranae IS UTILIZING BOTH AROMATIC AND ALIPHATIC HYDROCARBONS PRESENT IN THE THERMAL DIFFUSION FRACTIONS FROM THESE ASPHALTS, WHEREAS Pseudomonas 196Aa IS ABLE TO GROW ON ONLY THE n-ALKANES PRESENT IN THE FRACTIONS. A FURTHER POINT IS THAT Pseudomonas 196Aa IS NOT ABLE TO UTILIZE THE n-ALKANE THAT ARE KNOWN TO BE PRESENT (INFRARED DATA) WHEN THE CONCENTRATION OF AROMATIC HYDROCARBON IS HIGH. THIS IN TURN WOULD ACCOUNT FOR THE ABILITY OF

Mycobacterium ranae TO DEGRADE THE UNFRACTIONATED ASPHALT, WHEREAS Pseudomonas 196Aa IS UNABLE TO MODIFY THE THREE ASPHALTS. THIS DATA WOULD FURTHER INDICATE THAT Mycobacterium ranae MODIFIES THE AROMATIC HYDROCARBON PRESENT IN THE ASPHALTS, WITH BUT MINOR ACTION ON THE SATURATED HYDROCARBONS.

SUMMARY

WE HAVE DEMONSTRATED THAT THE ORGANISMS CAPABLE OF ATTACKING BITUMENS ARE DIVERSE AND DO NOT FALL INTO A SPECIFIC TAXONOMIC GROUP. THE MICROBIAL ACTION OF BITUMENS SHOWS A SPECIFICITY THAT INVOLVES BOTH THE MICROORGANISM AND THE BITUMINOUS SUBSTRATE. SOIL BURIAL TESTS DEMONSTRATE THE MOISTURE REQUIREMENT FOR MICROBIAL ACTION AS WELL AS DIFFERENCES IN THE SUSCEPTIBILITY OF BITUMINOUS MATERIALS.

IN A LIMITED SERIES OF EXPERIMENTS IT WAS FOUND THAT THE NET EFFECT OF MICROBIAL ACTION ON THREE ASPHALTS WAS AN INCREASE IN THE VISCOSITY OF THE ASPHALTS. IT IS THEORIZED THAT THE INCREASE IN VISCOSITY IS DUE TO THE OXIDATION OF CERTAIN ASPHALT COMPOUNDS WHICH ARE ALSO IMPORTANT IN DETERMINING THE RHEOLOGICAL CHARACTERISTICS OF THE ASPHALTS.

PRELIMINARY STUDIES ON THE COMPONENTS OF ASPHALTS UTILIZED BY MICROORGANISMS INDICATE THAT BOTH THE AROMATIC AND SATURATED HYDROCARBONS ARE UTILIZED BY Mycobacterium ranae. THIS ORGANISM CAUSED A DRASTIC MODIFICATION OF THE VISCOSITY OF THREE ASPHALTS. IT WOULD APPEAR THAT THIS MODIFICATION IN RHEOLOGICAL CHARACTERISTICS IS CAUSED BY OXIDATION OF AROMATIC AND SATURATED HYDROCARBONS IN THE PETROLENE (PENTANE SOLUBLE MATERIAL) FRACTION OF THESE ASPHALTS. FURTHER STUDIES ARE TO BE CONDUCTED ON THE ASPHALTENES AND OTHER FRACTIONS FROM THESE THREE ASPHALTS.

ACKNOWLEDGMENTS

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ASPHALT OXIDIZING BACTERIA OF THE SOIL

JOHN O. HARRIS*

THE SOIL MUST BE CONSIDERED AS THE NATURAL HABITAT FOR HYDROCARBON UTILIZING BACTERIA. IN DETERMINING THE POSSIBLE ROLE THAT BACTERIA MIGHT PLAY IN DECOMPOSITION OF ASPHALT OR OTHER COMPLEX ORGANIC MATTER, THE ENVIRONMENT OF THE SOIL MUST RECEIVE CAREFUL ATTENTION.

SOIL CONDITIONS AT THE BOTTOM OF THE BACK-FILLED PIPELINE DITCH HAVE BEEN EXTENSIVELY STUDIED AND HAVE BEEN FOUND TO BE QUITE FAVORABLE FOR MICROBIAL DEVELOPMENT (3). THE DATA INDICATED HIGHER WATER CONTENT AT DITCH BOTTOM WHEN COMPARED WITH LESS COMPACT SOIL OR SEMI-DENSE AREAS IN THE BACK-FILL ABOVE THE PIPELINE, ALLOWING AEROBIC CONDITIONS.

SINCE HYDROCARBON BACTERIA, CAPABLE OF UTILIZING ASPHALT AS THEIR SOLE FOOD ENERGY SOURCE, WERE FOUND IN ALL LOCATIONS WITH WIDELY VARIED GEOGRAPHICAL AND CLIMATIC CONDITIONS (4), THE PRESENCE OF THESE HYDROCARBON UTILIZING TYPES IN NORMAL SOILS RAISES IMPORTANT ECOLOGICAL PROBLEMS AS TO THEIR NICHE IN NATURALLY OCCURRING ORGANIC TRANSFORMATIONS. THE DATA TO BE REPORTED DEAL WITH ASPHALT UTILIZING BACTERIA IN NORMAL SOILS RELATIVE TO THE TOTAL MICROBIAL POPULATION, THEIR NUMBERS AND TYPES IN SOILS WITH ASPHALT PRESENT AND, FINALLY, PROTECTIVE COATING FAILURE DUE TO MICROBIAL ACTIVITY.

MATERIALS AND METHODS

ASPHALTIC PROTECTIVE COATINGS USED TO STUDY BACTERIAL UTILIZATION WERE ALL COMMERCIALY-AVAILABLE PRODUCTS.

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PRECAUTIONS IN HEATING AND APPLICATION GIVEN BY MANUFACTURERS WERE OBSERVED IN ALL INSTANCES. ROUTINE BACTERIOLOGICAL EXAMINATIONS FOLLOWED STANDARD LABORATORY PROCEDURES (6) WITH NUTRIENT AGAR, JENSEN'S AGAR, AND MARTIN'S ROSE BENGAL AGAR USED FOR PLATE COUNTS OF "TOTAL" BACTERIA, ACTINOMYCETES, AND FILAMENTOUS FUNGI RESPECTIVELY. INCUBATION WAS FOR 5 DAYS AT 30° C. ESTIMATION OF HYDROCARBON UTILIZING BACTERIA WAS ACCOMPLISHED USING SERIAL DILUTIONS OF SOIL INTO A MINERAL-SALTS DODECANE LIQUID MEDIUM WITH TEN REPLICATES PER DILUTION (4).

OXYGEN UPTAKE BY SOILS FOLLOWED REGULAR WARBURG MANOMETRIC TECHNIQUES (7). FOUR GRAMS OF SOIL WERE USED PER RESPIRATION VESSEL, WITH MOISTURE CONTENT ADJUSTED TO 55% OF FIELD CAPACITY.

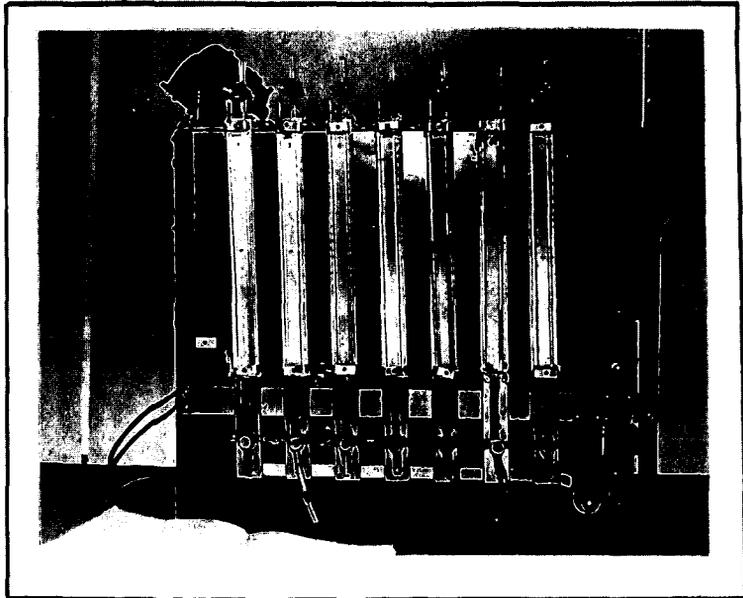


Fig. 1:--The Warburg microrespirometer shown here was used to show rapid oxidation of hydrocarbons by normal soil microorganisms.

RESULTS

CULTIVATED SOILS AND NON-CULTIVATED SOILS, SUCH AS PASTURES OR FORESTS, HAVE THEIR OWN CHARACTERISTIC MICROBIAL POPULATIONS. WITHOUT RIGOROUS IDENTIFICATION OF PURE CULTURES OR EXTENSIVE USE OF SPECIALIZED TECHNIQUES, SOIL POPULATIONS CAN BE EXPRESSED AS PLATE COUNTS OF BACTERIA, ACTINOMYCETES, AND FUNGI (6). ALTHOUGH THIS PROCEDURE GIVES ONLY RELATIVE INFORMATION, IT DOES GIVE INSIGHT AS TO THE OVER-ALL MICROBIAL ACTIVITY.

TABLE I
PLATE COUNT DATA OF

<u>SOIL</u>	<u>TOTAL BACTERIA</u> <u>(MILLIONS/GM/SOIL)</u>	<u>ACTINOMYCETES</u> <u>(MILLIONS/GM)</u>	<u>FUNGI</u> <u>(THOUSANDS)</u>	<u>HYDROCARBON</u> <u>BACTERIA</u> <u>(PER GRAM)</u>
1	50	6	390	870
2	14	2	123	23,000
3	179	45	360	1,160
4	44	11	20	1,300
5	65	4	48	223
6	24	5	330	5,420

PLATE COUNTS OF SIX NORMAL SOILS SHOW HYDROCARBON UTILIZING BACTERIA ARE A SIGNIFICANT PROPORTION OF THE TOTAL MICROBIAL POPULATION.

TABLE I SHOWS PLATE COUNT DATA FOR SIX NORMAL SOILS FROM NORTH CENTRAL KANSAS IN COMPARISON TO THE NUMBERS OF HYDROCARBON UTILIZING BACTERIA. THE COUNTS WERE MADE ON NON-FROZEN SURFACE SOIL IN FEBRUARY AND THUS REPRESENT THE EQUILIBRIUM SITUATION FOR WINTER WEATHER. OVER-ALL POPULATIONS WOULD BE HIGHER IN WARMER SOIL. BACTERIA CAPABLE OF GROWTH ON DECANE WERE PRESENT IN NUMBERS VARYING FROM 223 TO 23,000 PER GRAM

OF SOIL. IT SHOULD BE EMPHASIZED THAT NONE OF THESE SOILS HAD BEEN EXPOSED TO HYDROCARBONS WHICH WOULD CAUSE A SELECTIVE PRESSURE FOR THE DEVELOPMENT OF SPECIALIZED BACTERIA.

KESTER (5) PROPOSED THAT MOST, IF NOT ALL, ACTINOMYCETES CAN UTILIZE HYDROCARBONS. THE HIGH POPULATIONS OF THIS GROUP SHOWN IN TABLE I WOULD INDICATE THESE NORMAL SOILS WOULD HAVE A HIGH CAPACITY FOR THE UTILIZATION OF HYDROCARBONS. THE LIQUID SELECTIVE CULTURE USED TO ESTIMATE BACTERIAL GROWTH ON DODECANE WAS NOT FAVORABLE FOR ACTINOMYCETE DEVELOPMENT.

MARKED SEASONAL VARIATIONS OCCUR WITHIN THE MICROBIAL POPULATIONS IN THE UPPER LAYERS OF SOIL. TOTAL BACTERIA AND HYDROCARBON BACTERIA WERE DETERMINED DURING THE SPRING OF 1964 WHEN SOIL TEMPERATURES WERE GRADUALLY INCREASING, TO LEARN IF HYDROCARBON UTILIZERS COMPRISED A RATHER UNIFORM PERCENTAGE OF THE POPULATION AND WHETHER THIS GROUP RESPONDED TO MORE FAVORABLE GROWTH TEMPERATURES. POPULATION ESTIMATES

TABLE II
PLATE COUNT DATA OF

HC: HYDROCARBON
T: THOUSANDS
M: MILLIONS

DATE	<u>PASTURE SOIL</u>		<u>WHEAT FIELD</u>		<u>GARDEN SOIL</u>	
	BACTERIA	HC	BACTERIA	HC	BACTERIA	HC
	(M)	(T)	(M)	(T)	(M)	(T)
	<u>PER GRAM</u>		<u>PER GRAM</u>		<u>PER GRAM</u>	
MAR. 21	36	10	32	2	19	60
" 28	58	38	48	6	73	81
APR. 4	76	41	53	18	79	96
" 18	120	67	98	33	189	256
MAY 16	134	175	89	39	546	976
" 23	138	162	94	41	518	849

COMPARISON OF TOTAL BACTERIAL COUNTS WITH HYDROCARBON (HC) BACTERIA IN THREE SOILS AT SIX DATES DURING SPRING 1964.

FOR SIX DATES ARE SHOWN IN TABLE II FOR THREE TYPICAL SOILS. IN EACH SOIL HYDROCARBON TYPES INCREASED AS THE SOIL TEMPERATURES BECAME MORE FAVORABLE FOR GROWTH. THIS INCREASE IN POPULATION DUE TO TEMPERATURE (NOT SELECTIVE FOOD) INDICATES THAT THE ABILITY TO OXIDIZE PARAFFINIC MOLECULES SHOULD BE CONSIDERED A GENERAL RATHER THAN A SPECIALIZED PHYSIOLOGICAL CAPABILITY OF SOIL MICROORGANISMS (3).

FURTHER EVIDENCE THAT THE NORMAL SOIL POPULATION WAS ABLE TO OXIDIZE HYDROCARBONS RAPIDLY AND WITHOUT ADAPTATION CAME FROM SOIL RESPIRATION EXPERIMENTS. OXYGEN UPTAKE RATES WERE MEASURED OVER A 6-HOUR PERIOD IN WARBURG MICRORESPIROMETERS WITH 4 GRAMS OF SOIL TO WHICH WATER ONLY, 1% GLUCOSE, AND 1% DODECANE HAD BEEN ADDED.

COMPARISONS OF OXIDATIVE ACTIVITY ARE SHOWN IN FIG. 2.

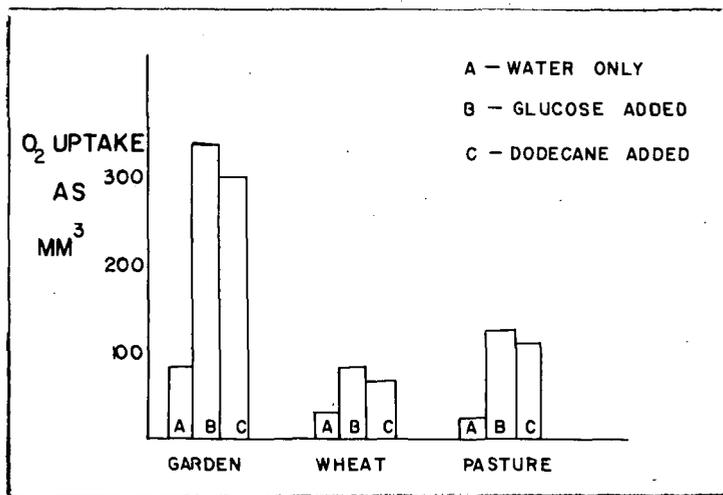


Fig. 2:--One per cent glucose, dodecane, or only water was added to normal soils. Total respiration as mm³ in six-hours interval shows dodecane readily oxidized by the normal soil population.

OXYGEN UPTAKE RATES FOR DODECANE ARE NEARLY AS RAPID AS THOSE FOR GLUCOSE. INDIVIDUAL SOIL DIFFERENCES ARE APPARENT. DATA IN FIG. 2 WERE FROM THE SAME SOIL SAMPLES AS SHOWN FOR MAY 16 IN TABLE II.

THUS THE RICH GARDEN SOIL WITH HIGHEST POPULATIONS GAVE THE HIGHEST OXYGEN UPTAKE RATES WITH BOTH SUBSTRATES TESTED. LIMITED DATA OF THIS TYPE HAS SHOWN THAT SOIL IN CONTACT WITH FAILING ASPHALT ROADS HAS EXTREMELY HIGH OXIDATIVE RATES (4). FURTHER RESEARCH ON RESPIRATION OF SOIL MAY GIVE VALUABLE INFORMATION REGARDING THE ROLE OF MICROORGANISMS IN DETERIORATION OF COMPLEX ORGANIC MOLECULES.

EARLIER PUBLICATIONS HAVE SHOWN QUITE HIGH POPULATIONS OF BACTERIA ASSOCIATED WITH FAILING ASPHALT ROADS (1) AND HAVE GIVEN EXTENSIVE DATA REPORTING HIGH BACTERIAL COUNTS IN SOIL NEAR PIPELINES (2). FROM FIELD INVESTIGATIONS ALONG OPERATING OIL AND GAS PIPELINES, DATA HAVE BEEN TAKEN FROM ONE HUNDRED BELL-HOLE INSPECTIONS OF ASPHALT COATED LINES. (ABNORMAL OR HIGHLY CORROSIVE SITUATIONS SUCH AS RIVER CROSSINGS, SWAMPS, LEAK SITES OR HIGH SALT SOIL WERE NOT INCLUDED.)

TABLE III COMPARES POPULATIONS OF BACTERIA CAPABLE OF GROWTH ON ASPHALT PRESENT IN SOIL ADJACENT TO THE ASPHALT COATING WITH THE NORMAL POPULATION IN UNDISTURBED VIRGIN SOIL OF THE RIGHT-OF-WAY (APPROXIMATELY 15 FT. TO 20 FT. FROM THE CENTER OF THE BACK-FILLED DITCH) AT THE SAME DEPTH. WITH THE NORMAL SOIL OVER 65% OF THE LOCATIONS HAD LESS THAN 100 HYDROCARBON BACTERIA, ONLY 2% HAD A COUNT OVER 1,000 AND NONE EXCEEDED ONE HUNDRED THOUSAND. WITH AVAILABLE FOOD FROM THE ASPHALT COATING, 34% HAD COUNTS BETWEEN TEN AND ONE HUNDRED THOUSAND, WHILE 10% HAD COUNTS IN EXCESS OF 100,000.

TABLE III

<u>HYDROCARBON BACTERIA PER GRAM OF SOIL</u>	<u>UNDISTURBED SOIL IN RIGHT-OF-WAY AT PIPELINE DEPTH</u>	<u>SOIL ADJACENT TO ASPHALT COATING</u>
LESS THAN 100	65%	10%
100 TO 1,000	21%	21%
1,000 TO 10,000	12%	25%
10,000 TO 100,000	2%	34%
MORE THAN 100,000	0%	10%

PERCENTAGES OF ONE HUNDRED ASPHALT COATED PIPELINES SHOWING VARIOUS POPULATION DISTRIBUTIONS OF ASPHALT UTILIZING BACTERIA.

THE KANSAS STATE UNIVERSITY RESEARCH PROJECT, ON WHICH THIS INFORMATION IS BASED, WAS STARTED IN 1956...WITH FIELD TRIPS EACH YEAR SINCE THEN TO EXAMINE MORE THAN 1,000 BELL-HOLE OPENINGS ALONG OPERATING OIL, GAS AND WATER PIPELINES.

THESE BELL-HOLE OPENINGS WERE DUG AND MADE AVAILABLE BY THE PERSONNEL OF THE COOPERATING PIPELINE COMPANIES. SOIL SAMPLES WERE ANALYZED IN THE LABORATORY FOR BACTERIAL AND MOISTURE CONTENT AT DIFFERENT LEVELS OF THE BACK-FILLED DITCH, PLUS pH VALUES, AND THE IDENTIFICATION OF SOILS BY TYPE.

THE INFORMATION AND DATA ACCUMULATED DEMONSTRATES THAT BECAUSE OF THE MIXING OF SOILS DURING THE BACK-FILLING OPERATION (AFTER THE PIPE IS LOWERED-IN), THE BACK-FILLED DITCH BECOMES A MAN-MADE ENVIRONMENT, WHICH PROVIDES IDEAL CONDITIONS FOR BACTERIAL DEVELOPMENT AND ALSO FOR THE ACCUMULATION OF SOIL WATER. COMPARING THE ANALYSES OF SOIL SAMPLES TAKEN AT THE SAME DEPTHS IN THE VIRGIN SOIL OF THE RIGHT-OF-WAY AND IN THE BACK-FILLED DITCH PROVES THAT THERE

MUST BE TAKEN INTO CONSIDERATION THE DIFFERENCE IN THE BACTERIAL POPULATIONS AND SOIL WATER CONTENT, BOTH OF WHICH ARE MANY TIMES LESS IN THE RIGHT-OF-WAY THAN IS FOUND IN A PIPELINE DITCH.

SAMPLES OF MANY TYPES OF COATING SYSTEMS WERE REMOVED FROM THE PIPE AND ANALYZED IN THE LABORATORY FOR MOISTURE AND BACTERIAL CONTENT. DATA WAS RECORDED INDICATING THE CONDITION OF THE BOND OF THE COATINGS, CONDITION OF PIPE SURFACE (RE CORROSION, RUSTING AND/OR PITTING), YEARS OF UNDERGROUND SERVICE, USE OF CATHODIC PROTECTION, AND OTHER PERTINENT INFORMATION FOR FINAL EVALUATION PURPOSES.

DURING THE FIELD TRIPS OF THIS COAST-TO-COAST SURVEY IT WAS APPARENT THAT LABORATORY EXAMINATION AND ANALYSES OF THE COATINGS MUST BE MADE TO DETERMINE THE AMOUNT OF BACTERIAL AND MOISTURE PENETRATION IN THE COATINGS, FROM THE SOIL SURROUNDING THE COATED PIPE. DATA HAS BEEN TABULATED (TABLE IV) TO SHOW THE ANALYSES OF THE ASPHALT COATINGS SECURED IN REPRESENTATIVE GEOGRAPHICAL AREAS OF THE UNITED STATES.

FURTHERMORE, THE FIELD DATA, TOGETHER WITH CONSULTATIONS WITH CORROSION ENGINEERS OF THE COOPERATING OIL AND GAS PIPELINES, LED TO THE CONCLUSION THAT BACTERIAL NUMBERS, WATER PENETRATION INTO THE COATING, WATER IN THE SOIL NEXT TO THE PIPE, YEARS OF EXPOSURE TO THE SOIL AND IN DIFFERENT SOIL TYPES MUST BE CONSIDERED. A COMBINATION OF ALL OF THESE IMPORTANT FACTORS DETERMINE COATING PERFORMANCE.

THE DATA IN TABLE IV SHOWS THE BACTERIAL COUNT PER GRAM EACH OF TWO ASPHALT COATING SAMPLES THAT WERE REMOVED FROM OPERATING PIPELINES FOR COMPARATIVE PURPOSES AND SHOWS THE PENETRATION OF THE BACTERIA INTO THE COATING SAMPLES. (SEE THE COUNTS TABULATED UNDER SAMPLE #2.) ALSO INCLUDED IS A

TABULATION OF MOISTURE CONTENT DETERMINED (BY THE DEAN-STARK A.S.T.M. METHOD) ON THE SAME TWO COATING SAMPLES.

TAKING ONLY ONE COATING SAMPLE WOULD NOT REVEAL ANY PENETRATION IN THE PORTION OF THE COATING FILM NEXT TO THE PIPE SURFACE. THEREFORE A TECHNIQUE WAS DEVELOPED FOR TAKING COATING SAMPLE #2, BY REMOVING THE OUTER HALF OF THE COATING.

COATING SAMPLE #1: TOTAL SAMPLES WERE REMOVED, AS FOUND ON THE PIPE WHEN UNCOVERED.

COATING SAMPLE #2: THIS SAMPLE WAS SECURED AFTER APPROXIMATELY ONE-HALF (1/2) OF THE THICKNESS OF THE ORIGINAL COATING SYSTEM WAS REMOVED BY SKIVING (WITH DRAW KNIFE). THEN THIS SAMPLE WAS REMOVED FROM THE PIPE. THIS METHOD WAS DEVELOPED TO ELIMINATE: ANY TRAPPED SOIL OR ORGANIC MATTER IN WRINKLES DUE TO SOIL STRESS, IRREGULAR SURFACES, ETC....ALSO TO ELIMINATE WRAPPING MATERIALS THAT CONTAIN ORGANIC SUBSTANCES WHICH ARE SUBJECT TO MICROBIAL GROWTH.

TABLE IV

ASPHALT COATING				% WATER PENETRATION COATING		Years Underground Service	% Soil Moisture Next to Pipe
Sample No. 1		Sample No. 2		Sample No. 1	Sample No. 2		
Aerobes	Anaerobes	Aerobes	Anaerobes				
CENTRAL OHIO							
32,000	None	4,100	None	1.6	1.6	3	23.4
38,000	1,100	8,600	+300	1.6	1.6	3	28.3
380,000	12,000	36,000	800	1.8	1.8	3	19.4
420,000	17,000	19,000	11,000	1.6	1.6	3	52.1
18,000	2,100	2,940*	350*	1.8	1.8	7	32.8
PENNSYLVANIA							
4,800,000	89,000	2,600,000*	42,000*	7.6	5.9	6	44.7
CENTRAL KANSAS							
4,300,000	23,000	600,000*	19,000*	16.0	12.1	18	19.3
440,000	31,000	73,000*	11,000*	14.9	10.9	18	22.0
NEBRASKA							
190,000	1,000	84,000*	1,100*	15.2	11.6	12	33.6
1,080,000	34,000	63,000*	13,000*	14.6	11.9	20	19.8
590,000	3,000	410,000*	+200*	12.4	11.2	21	31.6
OKLAHOMA							
1,500,000	400,000	3,000*	+100*	11.2	7.1	9	25.0
1,250,000	280,000	78,000	19,500	12.1	9.3	9	29.0
MISSISSIPPI							
2,500	+300	600*	+200*	1.5	1.5	5	27.2
5,000	+100	1,700*	+100*	1.5	1.5	5	15.2
15,500	+100	+200*	+100*	1.5	1.5	5	26.6
1,500	+100	1,000*	+100*	3.0	3.0	5	30.0
SOUTH TEXAS							
1,400	None	800	None	1.8	1.8	6	10.3
24,000	1,000	5,000	600	2.2	2.2	6	23.4
12,000	None	8,000*	None*	9.3	9.2	12	33.3
NORTHWEST TEXAS							
30,000	1,300	11,000*	5,000*	19.5	15.7	10	23.6
58,000	6,000	109,000*	600*	18.0	18.0	10	29.2
6,100*	6,000	1,100*	4,500*	19.0	19.0	9	32.5
88,000	4,700	9,900*	3,900*	4.3	4.2	12	11.2
100,000	4,200	18,000*	2,900*	8.0	8.2	9	22.0
106,000	20,000	107,000*	3,900*	9.3	9.2	12	27.2
1,330,000	2,400	72,000*	1,700*	19.5	15.3	11	37.0
SOUTHWEST TEXAS							
50,000	300	160,000*	3,300*	14.2	13.6	10	41.6
39,000	500	43,000*	200*	11.6	11.6	10	28.6
420,000	6,000	516,000*	3,000*	12.8	11.8	9	39.6
146,000	18,000	304,000*	28,000*	5.2	3.2	7	28.3
300,000	43,000	180,000*	41,000*	18.0	15.8	16	19.4
FAR WEST TEXAS							
290,000	12,000	180,000*	9,000*	18.0	18.0	12	21.0
267,000	69,000	210,000*	51,000*	19.0	19.0	11	22.0
4,100,000	360,000	390,000*	410,000*	8.0	8.0	4	14.9
SOUTHERN CALIFORNIA							
1,148,000	1,300	510,000*	300*	4.3	4.2	7	9.9*
320,000	7,000	95,000*	2,000*	14.1	10.9	12	21.9
3,500	2,000	2,000*	1,500*	16.2	12.2	19	25.3
78,000	+100	15,000*	+100*	9.8	9.9	16	4.2*
2,800,000	17,000	2,600,000*	19,000*	7.6	7.6	15	11.6*
3,400,000	20,000	4,800,000*	18,000*	9.3	9.2	7	13.7*
CENTRAL CALIFORNIA							
24,000	2,000	3,500*	2,000*	5.3	5.1	7	5.5
9,500	3,000	8,000*	3,500*	4.1	5.1	10	2.8*
3,600,000	6,000	3,000,000*	6,000*	3.1	3.1	9	7.0
4,000,000	6,000	1,900,000*	5,000*	6.1	6.1	20	3.1*
75,000	4,000	30,000*	1,000*	8.1	8.1	7	4.2
430,000	4,000	40,000*	7,000*	14.3	10.7	11	26.6
UTAH							
8,380,000	17,000	1,740,000*	21,000*	6.6	6.6	7	12.4
1,480,000	1,000	184,000*	500*	11.8	11.4	18	12.8
58,000	+100	30,000*	+100*	14.3	14.3	6	9.9
660,000	300	54,000*	300*	4.1	4.1	6	28.2
NEW MEXICO							
260,000	17,000	+200	800	6.5	6.5	10	8.7*
450,000	130,000	51,000*	12,500*	9.6	9.6	10	18.7*
ARIZONA							
1,260,000	45,000	2,000,000*	60,000*	8.2	8.3	10	39.2
2,800,000	88,000	140,000*	40,000*	8.2	8.2	10	28.2

* Unbonded

* Surface Soil Moisture <1.0%

ELECTRON MICROGRAPHS, FIGS. 3 AND 4, ILLUSTRATE THE TYPICAL MICROSCOPIC APPEARANCE OF TWO MICROORGANISMS COMMONLY FOUND IN NORMAL UNDISTURBED SOILS IN CONTINENTAL NORTH AMERICA. ALSO LARGE NUMBERS HAVE BEEN CULTURED FROM ASPHALT COATINGS AND FROM THE SOIL SURROUNDING COATED PIPELINES.

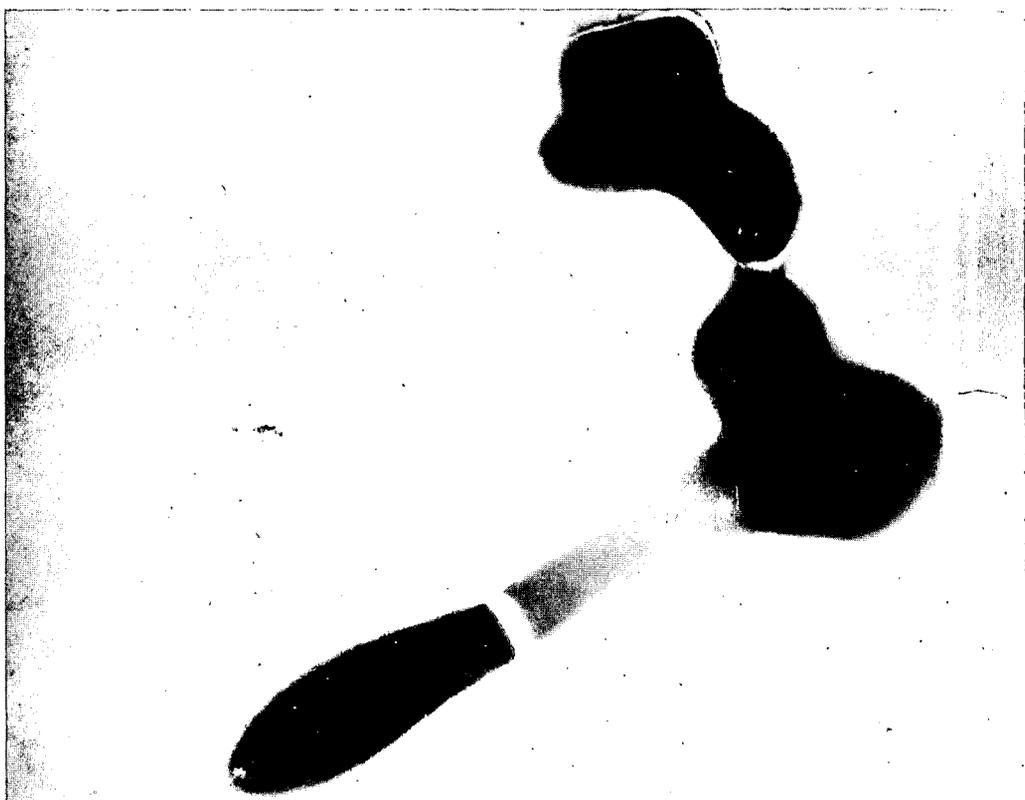


Fig. 3:--53,200 magnification. Pleomorphic rod-shaped cells, commonly seen in species of Nocardia, a common type of actinomycete isolated from asphalt coatings. Moisture under the coating -- some pitting -- anaerobic corrosion on the pipe -- no bond of coating -- 10 years' underground service. In these bacteria, branch forms may be seen, with swollen and club-shaped rods.

BOTH TYPES OF BACTERIA GREW WELL IN PURE CULTURES IN THE LABORATORY WHEN ASPHALT, OR A WIDE VARIETY OF LIQUID OR SOLID HYDROCARBONS WERE THE SOLE SOURCE OF ENERGY AND FOOD FOR THE DEVELOPING CELLS.



Fig. 4:--16,500 magnification. Medium-size rods, members of genus *Pseudomonas*, isolated from both asphalt coating and soil surrounding the pipe. Coating separated from pipe at several locations -- severe pitting -- 14 years' underground service -- coating sample this location, 370,000 aerobes, 560,000 anaerobes, moisture content 16.4%.

SUMMARY

BACTERIA CAPABLE OF GROWTH ON PARAFFINIC HYDROCARBONS ARE NORMAL INHABITANTS OF THE SOIL. POPULATIONS OF BACTERIA WITH THESE CAPABILITIES MAY VARY FROM SEVERAL HUNDRED TO THOUSANDS PER GRAM OF SOIL. ACTINOMYCETES COMMONLY ATTAIN COUNTS OF MILLIONS PER GRAM. RESPIRATION MEASUREMENTS SHOWED DODECANE IMMEDIATELY AND RAPIDLY OXIDIZED BY "NORMAL" SOIL, INDICATING LARGE POPULATIONS WITH THIS PHYSIOLOGICAL ABILITY. COUNTS OF ASPHALT-UTILIZING BACTERIA SHOWED MUCH HIGHER POPULATIONS IN SOIL ADJACENT TO COATED PIPELINES THAN IN UNDISTURBED SOIL OF THE RIGHT-OF-WAY AT THE SAME DEPTH.

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