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.

PRIMERS

Primers for the enamels must be capable of application by spraying, rolling, or brushing. They must dry in a reasonalbe 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.

APPLICATION

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.

MILL APPLICATION

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 in 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	PLASTICIZED AWWA	PLASTICIZED 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, 77 F.	ASTM D 71	1.40 - 1.60	1.40 - 1.60	1.40 - 1.60	1.40 - 1.60	1.40 - 1.60
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
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 corrosings, etc.*

TABLE 3

ELECTRICAL RESISTIVITY OF SPECIMENS OF ENAMELS

imersed 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.

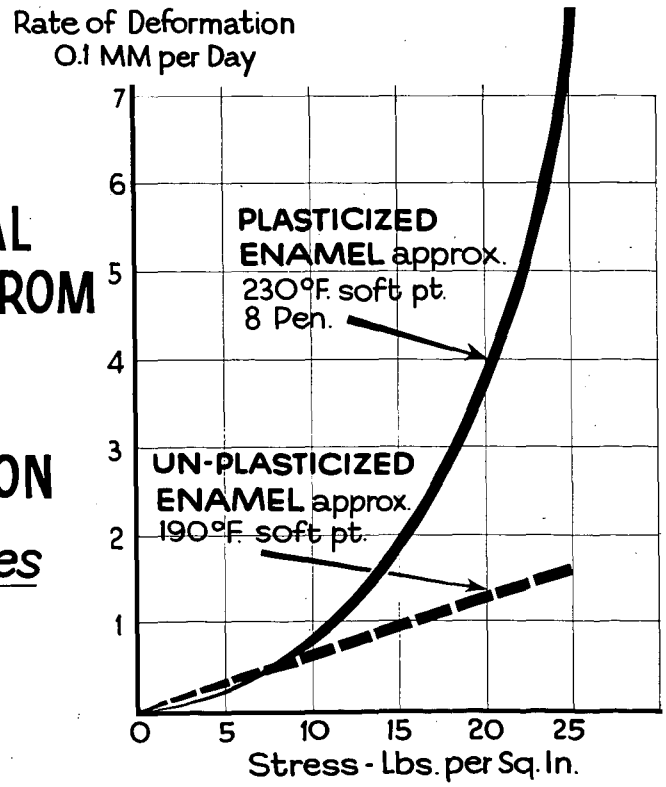


FIGURE 2

RHEOLOGICAL DIAGRAM FROM BLUNT ROD PRESSURE DEFORMATION

Test Values at 115°F

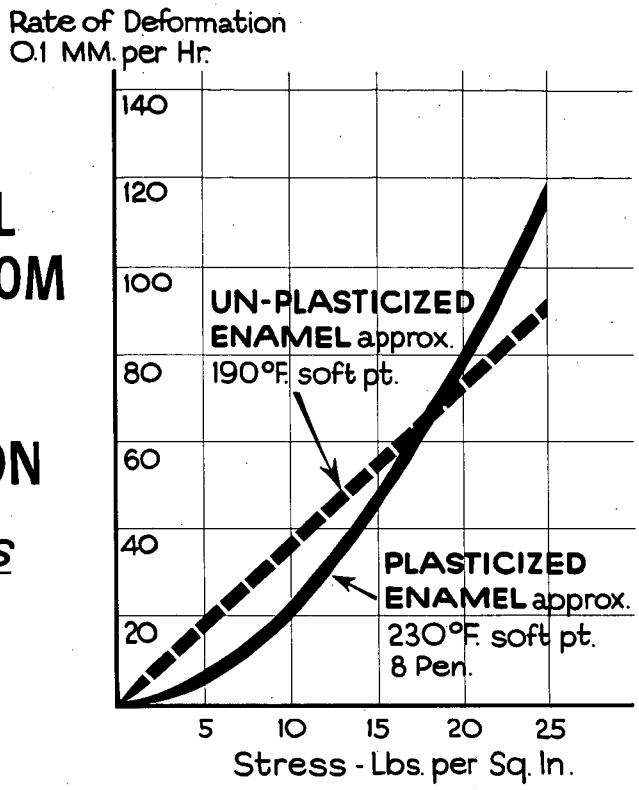
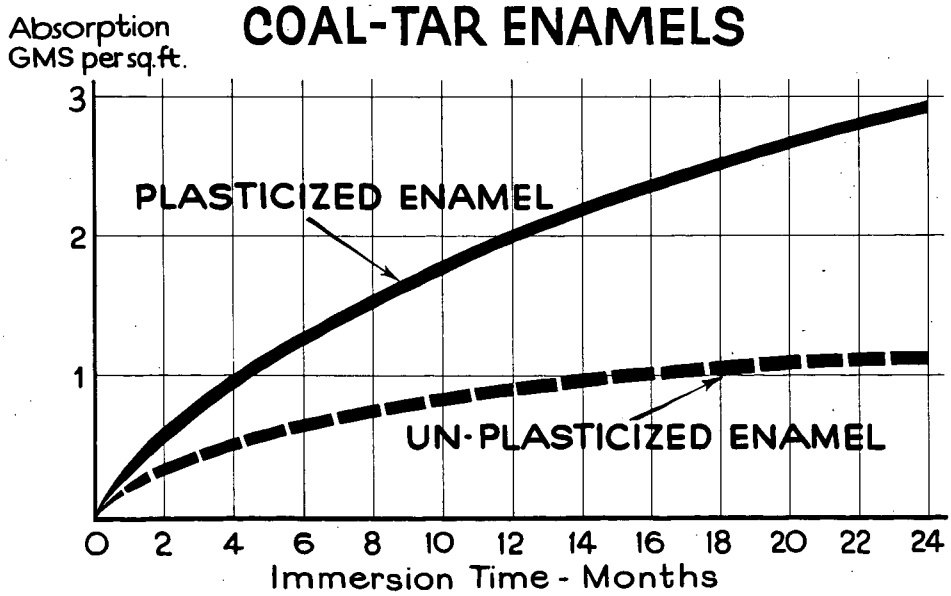


FIGURE 3

WATER ABSORPTION COAL-TAR ENAMELS



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 climes.

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 electrochemical cell. Some of the chemical reactions that are promoted by its negative character are:

In aerated nearly neutral soils oxygen reduction can occur:

$$1/2\ O_2 + H_2O + 2e \longrightarrow 2OH^-$$

In acid soils the hydrogen ion is reduced:

$$2H^+ + 2e \longrightarrow H_2$$

Because the hydrogen ion has such a great affinity for H_2O [2] the more complete picture is:

$$2H_2O \cdot H^+ + 2e \longrightarrow H_2 + 2H_2O$$

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 imidazolinium 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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9. U.S. Patent No. 3,070,524.
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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:

Ingredients	g./l. of H_2O
Magnesium Chloride - $6H_2O$	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 $\pm$ 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" ± 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° 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 $\pm$ 5° 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
	Settlement ratio [filler], AASHO T 109-42 [modified]	1.10 at 400° F
Indicating Coated Pipe Handling and Storage Chracteristics	Flow resistance [rod deformation], Asphalt Institute[2]	15 mils, 6 hrs., 115° F
	Low temperature crack resistance, Asphalt Institute[3]	Pass to 0° F
	High temperature sag resistance, Asphalt Institute[3]	160° F+
	Impact resistance, [Southern California Gas Company procedure [modified]]	Pass to 32° F
Indicating Coating Performance in Service	Flow resistance [rod deformation], Asphalt Institute[2]	15 mils, 6 hrs. 115° F
	Low temperature crack resistance, Asphalt Institute[3]	Pass to 0° F
	Cathodic disbonding resistance, sq. inches[1]	0.03-0.5 7-day test[4]
	Electrical resistance, ohm-cm[1]	$1 \times 10^{15+}$
	Water absorption, wt. percent[1]	1.0 in 35 weeks
Indicating Uniformity	Penetration at 77° F, ASTM D-5	7
	Softening point, ASTM D-36	240
	Ash [mineral filler], wt.%, ASTM D-482 [modified]	20
	Weight, pounds per gallon, ASTM D-71	10
Determining coverage rate per unit of weight	Weight, pounds per gallon, ASTM D-71	10

[1]Test procedure given in the appendix

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

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

[4]This property is quite dependent upon the primer used.

TABLE II

PRIMER FOR HOT-APPLIED ASPHALT PIPE COATING - TYPICAL PROPERTIES

Property	Typical Value
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

Primer	Coating	Disbonded area 7 days, -1.5 volts, sq. in.
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]

Additive		Disbonding		
Trade Name	Compound Type	Area, in.^{2} Primer + Additive	Area, in.^{2} Primer [Control]	Ratio, Additive Primer/ Control
Nalquat G-8-13	1,[2-Hydroxethyl]-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	Alkoxylated 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

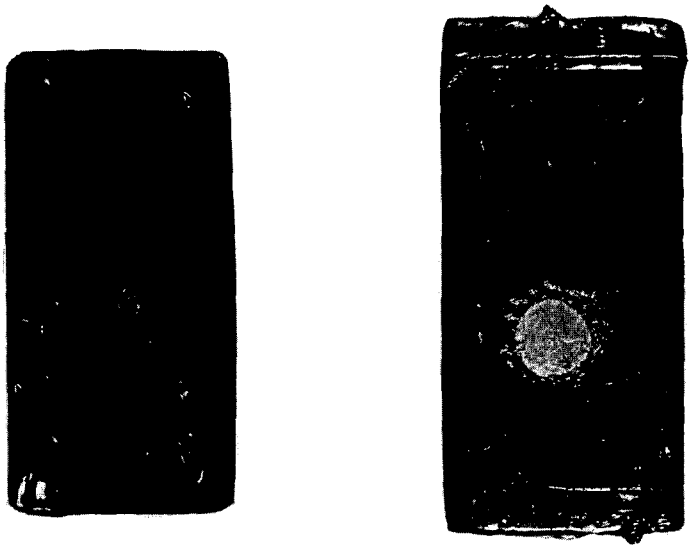

FIGURE I

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

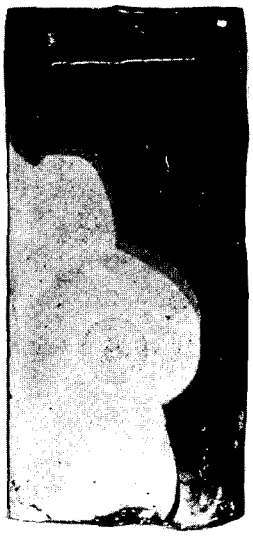

FIGURE 2

COATING COLD FLOW FROM HYDROGEN PRESSURE
IN CATHODIC DISBONDING TEST

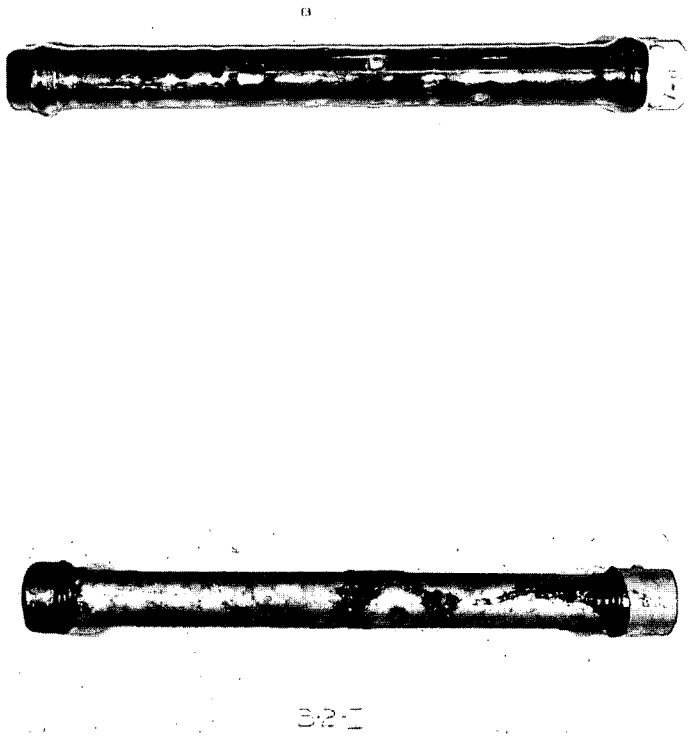

FIGURE 3

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

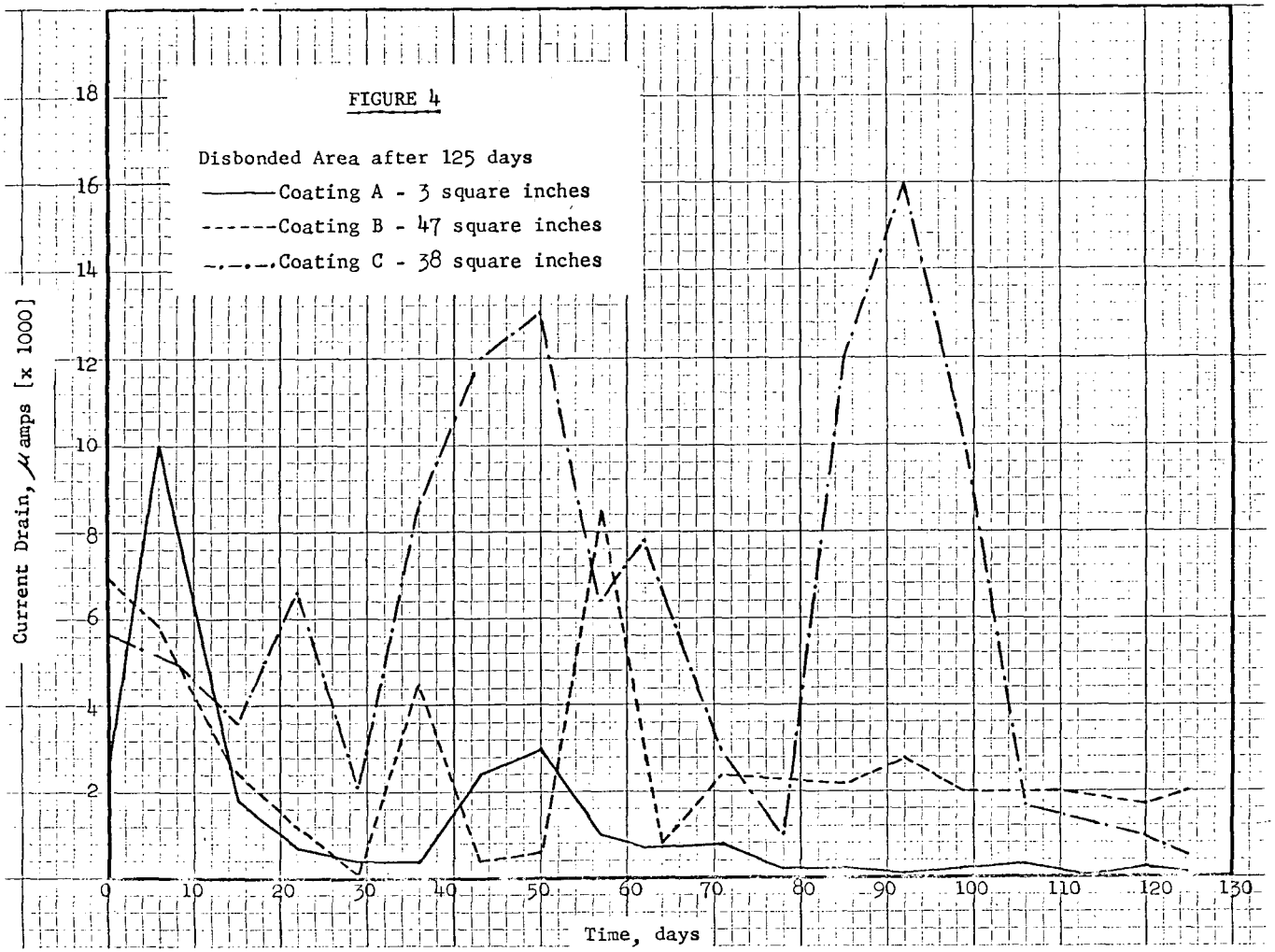
FIGURE 4
Disbonded Area after 125 days
Coating A - 3 square inches
Coating B - 47 square inches
Coating C - 38 square inches
Current Drain, μ amps [x 1000]
18
16
14
12
10
8
6
4
2
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Time, days

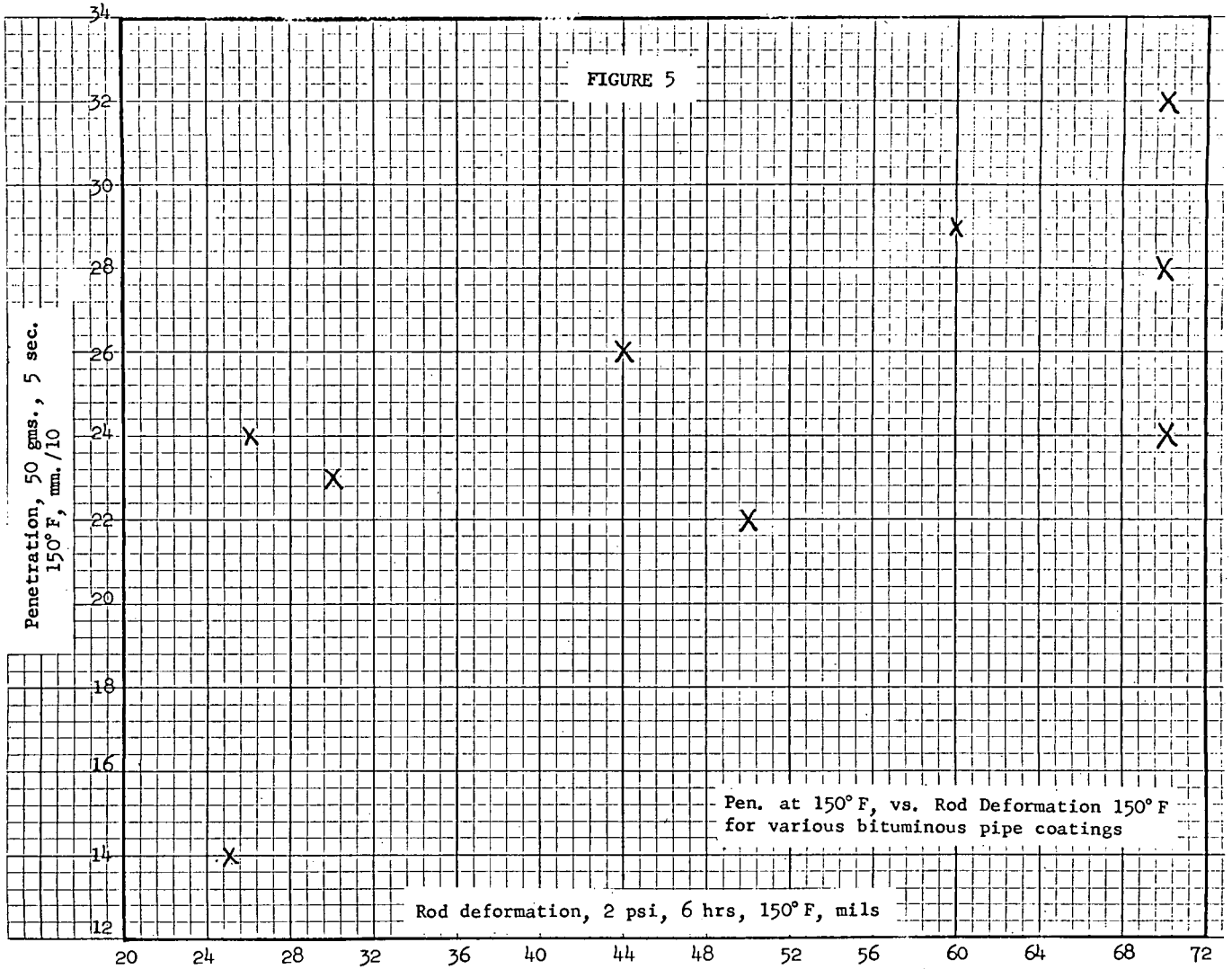
FIGURE 5
Penetration, 50 gms., 5 sec. 150° F, mm./10
34
32
30
28
26
24
22
20
18
16
14
12
20
24
28
32
36
40
44
48
52
56
60
64
68
72
Rod deformation, 2 psi, 6 hrs, 150° F, mils
Pen. at 150° F, vs. Rod Deformation 150° F
for various bituminous pipe coatings

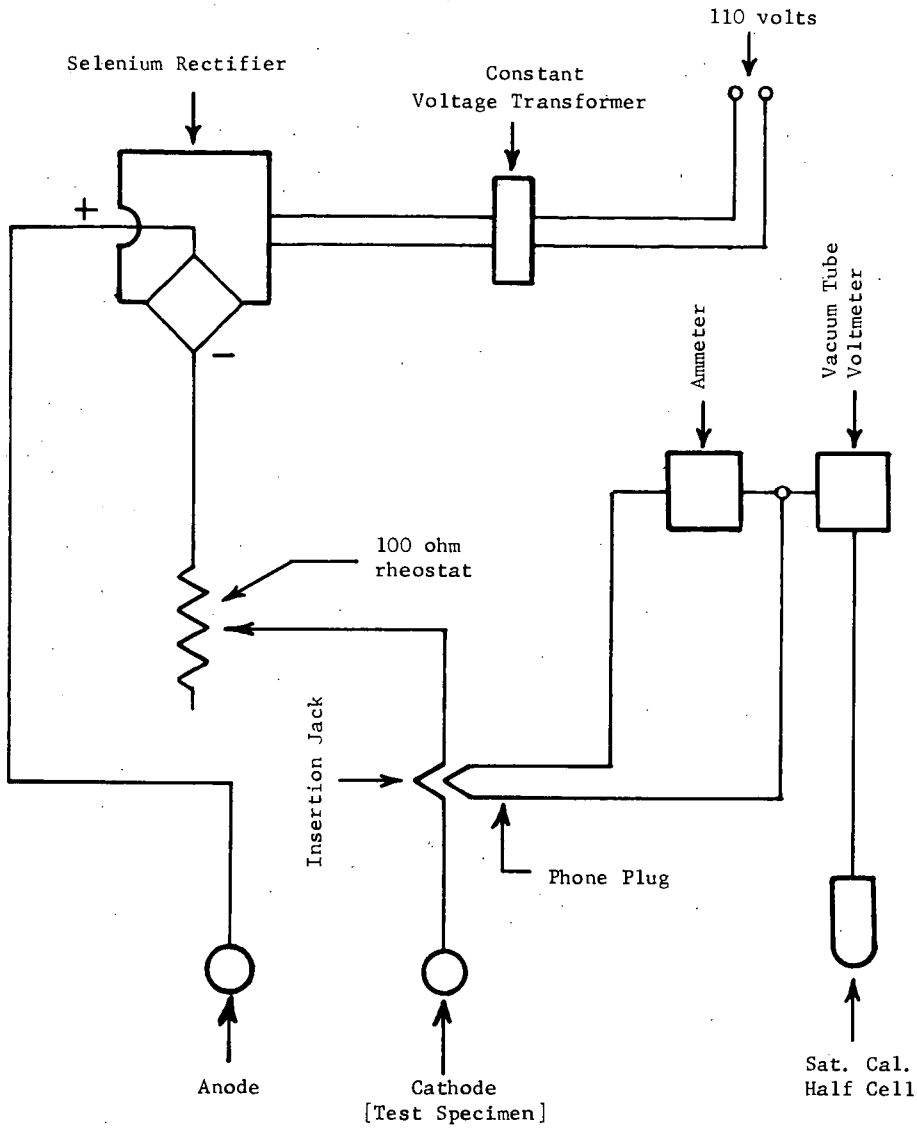

FIGURE I - APPENDIX

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 alligatoring. 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

	Type a Military Spec. No. MIL-P-6883 Aug. 1950 Supersedes AN-P-31a	Type b American Water Works Association AWWA D 102-62 T Sec. 3.11
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 1 Hr. to Touch 8 Hrs. to Handle	After 24 hours at 77°F. and flushing shall impart no objectionable taste or odor to water
With Aluminum Powder	1.3#/Gallon	Shall contain no added filler, pigments, fibrous materials or asphalt.

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 alligatoring 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)

Component A

Ingredient	% by Wt.	Lbs. for 3.5 Gal. Batch	Gal.
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

Ingredients	% by Wt.	Lbs. for 3.5 Gal. Batch	Gal.
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
	100.0	38.50	3.50

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

Component B

Liquid Epoxy Resin (99% N.V. Epoxide Equivalent)	-	9.7	1.0

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)

	Per Cent by Weight
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 resistancd 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, alkalies, 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 o.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 waterlogged 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 ues 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. $\frac{1}{2}$ 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)

Product	Typical Usage Dry Film Thickness, Inches	Perms at 77°-55°F
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 time[3]. 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 measured[4]. 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 cm^3 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 Lee[5]. 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. Elm[6] 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. Arthur[7] 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 Smith[8] 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 Seaberg[9] 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 Kingsbury[10] 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_o) for the whole coating insulation is calculated by using the following equations for parallel circular plate capacitors:

$$C_o = \frac{.0885\ K_o \cdot S}{t} \qquad\qquad K_o = \frac{C_o\ t}{.0885 \cdot S}$$

Where in the above; (initial capacitance reading) C_o is in micro micro farads (MMfd.), K_o 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.

The total capacitance $C = \frac{C_1 \quad C_2}{C_2 + C_1}$

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_o 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:

$$t = t_1 + t_2$$

$$t_2 = t - t_1$$

$$\frac{1}{C} = \frac{t_1}{.0885 \cdot 81 \cdot S} + \frac{t - t_1}{.0885 \cdot K_2 \cdot S}$$

$$\frac{1}{C} = \frac{t_1}{7.1685\ S} \quad \frac{t - t_1}{.0885 \cdot K_2\ S}$$

The value for K_2 is the same as for K_o at the start of the test when $t_1 = 0$ i. e.

$$C_o = \frac{.0885 \cdot K_2 \cdot S}{t} \quad \text{and } K_2 = \frac{C_o\ t}{.0885 \cdot S}$$

Then, substituting for K_2:

$$\frac{1}{C} = \frac{t_1}{7.1685 \cdot S} + \frac{t - t_1}{\frac{C_o\, t}{.0885 \cdot S}\,(.0885 \cdot S)}$$

$$\frac{1}{C} = \frac{t_1}{7.1685 \cdot S} + \frac{t - t_1}{C_o \cdot t}$$

$$7.1685\, C_o \cdot S \cdot t + C \cdot C_o \cdot t \cdot t_1 + 7.1685\, C \cdot S\, (t - t_1)$$

$$7.1685\, C_o \cdot S \cdot t = C \cdot C_o \cdot t \cdot t_1 + 7.1685\, C \cdot S \cdot t - 7.1685\, C \cdot S \cdot t_1$$

$$t_1\, (C \cdot C_o t - 7.1685\, C \cdot S) = 7.1685\, C_o \cdot S \cdot t - 7.1685\, C \cdot S \cdot t$$

$$t_1 = \frac{7.1685 \cdot S \cdot t\, (C_o - C)}{C \cdot C_o t - 7.1685\, C \cdot S}$$

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_o 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_o 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 ifself 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 Koenecke[14], 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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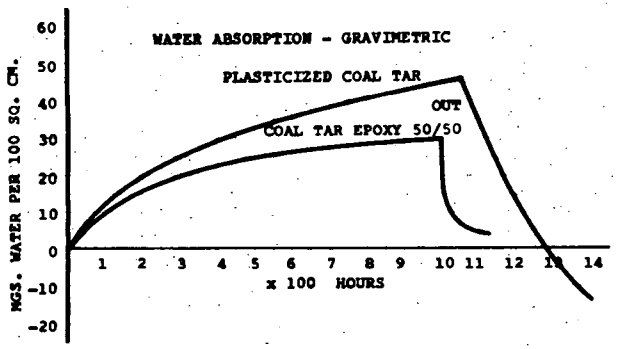


Fig. 1

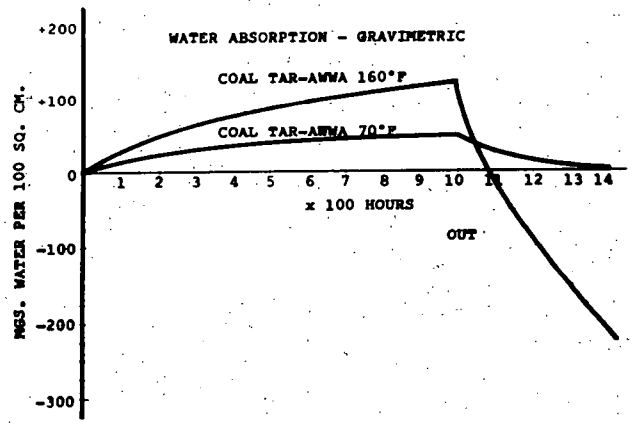


Fig. 3

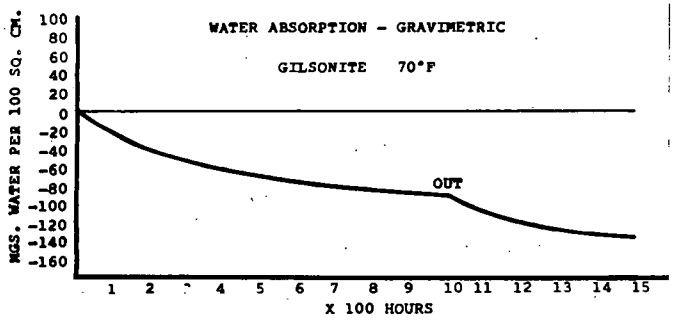


Fig. 2

WATER ABSORPTION - GRAVIMETRIC

MGS. PER 100 SQ. CM. PER 1000 HOURS IMMERSION - TAP WATER
VOLUME RESISTIVITY = 70000 (OHMS)

TYPE	MG. GAIN AT 70°F	LOSE ON DRYING	MG. GAIN 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)	38	0.0	184.00	0.00
ASPHALT H 220°F (HOT-APPLIED)	39	0.0	270.00	0.00
COAL TAR PLASTICIZED ENAMEL AWWA (HOT-APPLIED)	40	-5.0	120.00	-346.00
COAL TAR STANDARD ENAMEL PITCH (HOT-APPLIED)	40	-7.0	—	—
ASPHALT-STYRENE (COLD-APPLIED)	40	-42.0	438.00	-187.00
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	1053.00	0.00
ASPHALT K 220°F (HOT-APPLIED)	47	0.0	556.00	0.00
ASPHALT H2 220°F (HOT-APPLIED)	49	0.0	533.00	0.00
ASPHALT E 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	-31.00	-200.00
COAL TAR-NITRILE COATING (COLD-APPLIED)	83	-7.0	3800.00	-423.00
COAL TAR MASTIC CA-50 (COLD-APPLIED)	107	-208.0	1400.00	-730.00

Fig. 4

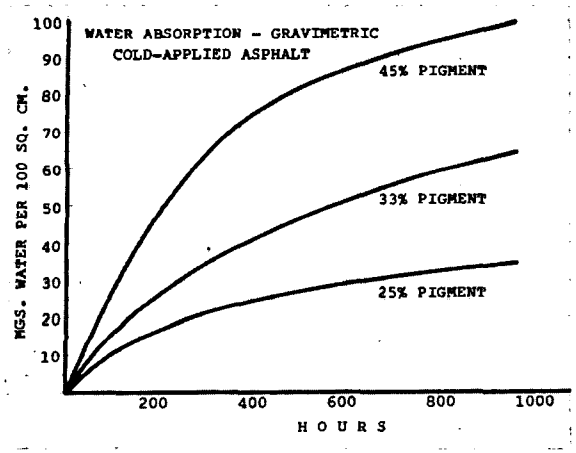
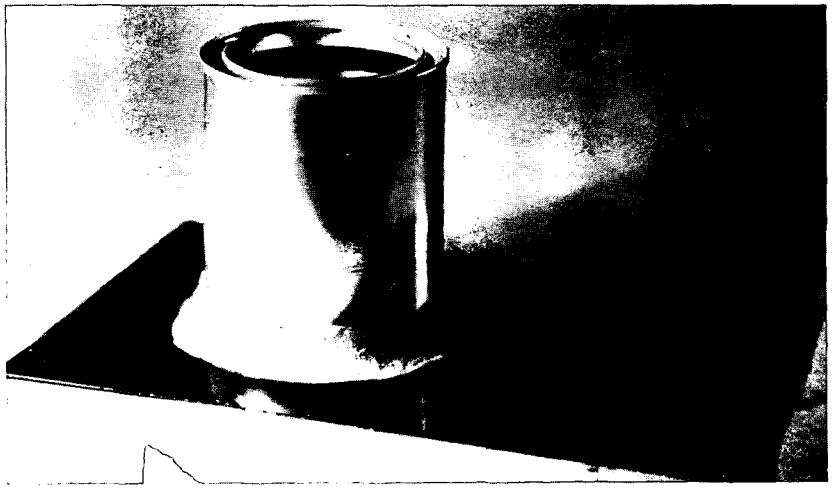


Fig. 5



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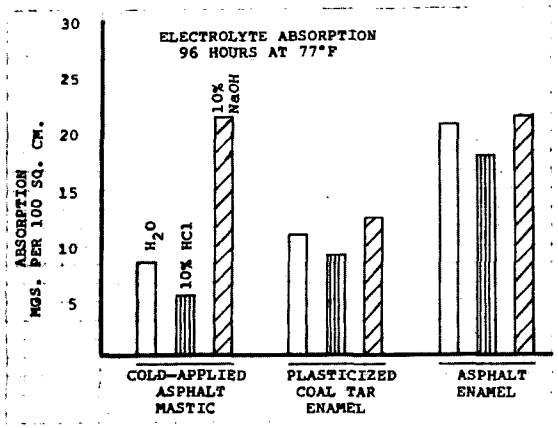

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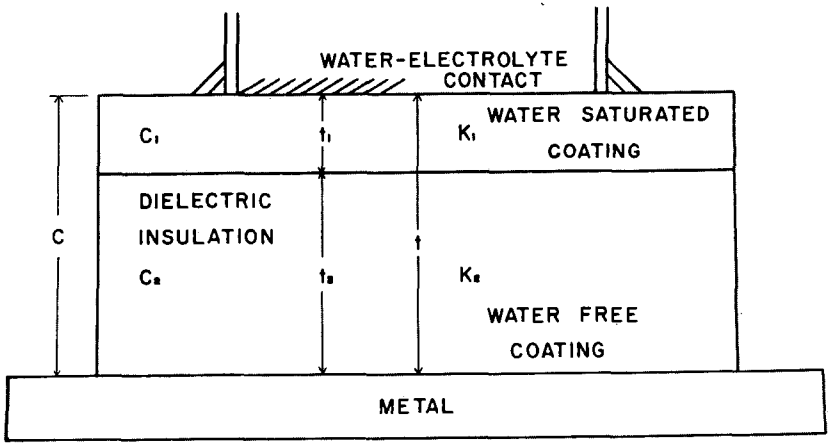


Fig. 8

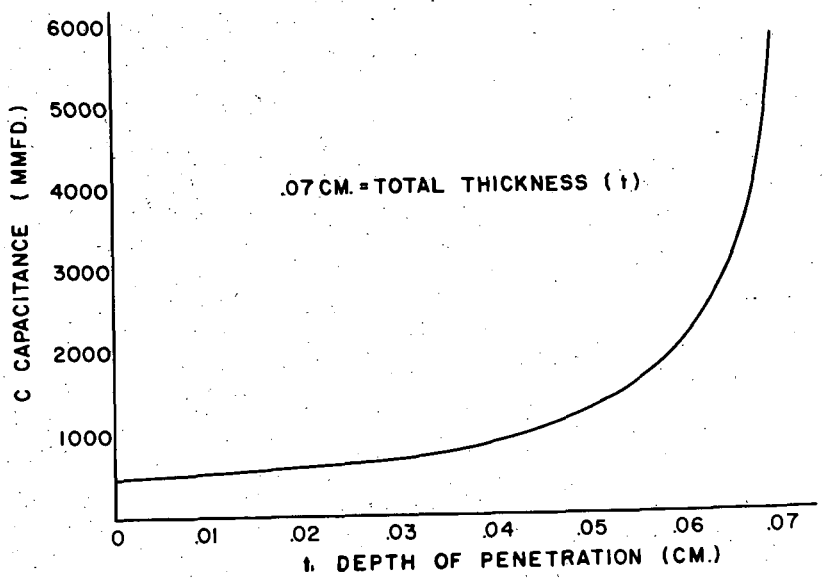
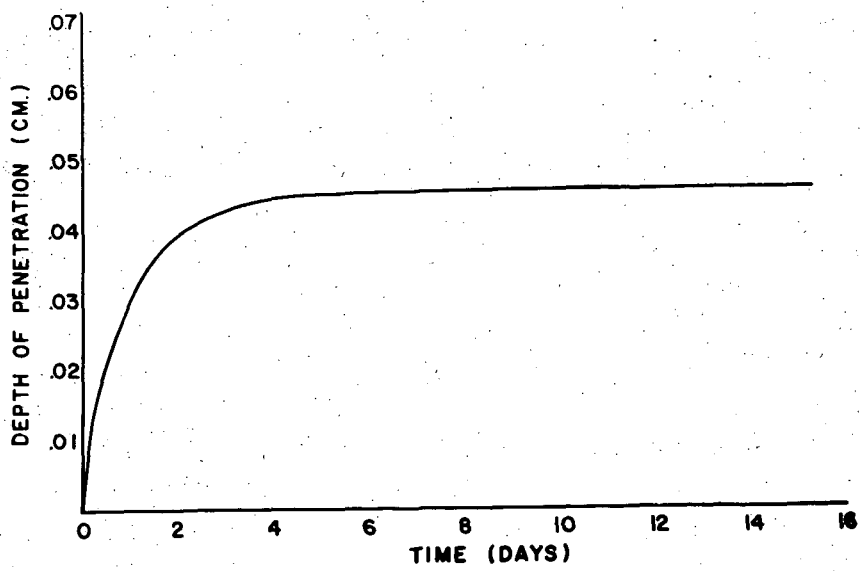

6000
5000
4000
3000
2000
1000
C CAPACITANCE (MMFD.)
.07 CM. = TOTAL THICKNESS (t)
0
.01
.02
.03
.04
.05
.06
.07
t, DEPTH OF PENETRATION (CM.)

Fig. 9


.07
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.01
DEPTH OF PENETRATION (CM.)
0
2
4
6
8
10
12
14
16
TIME (DAYS)

Fig. 10

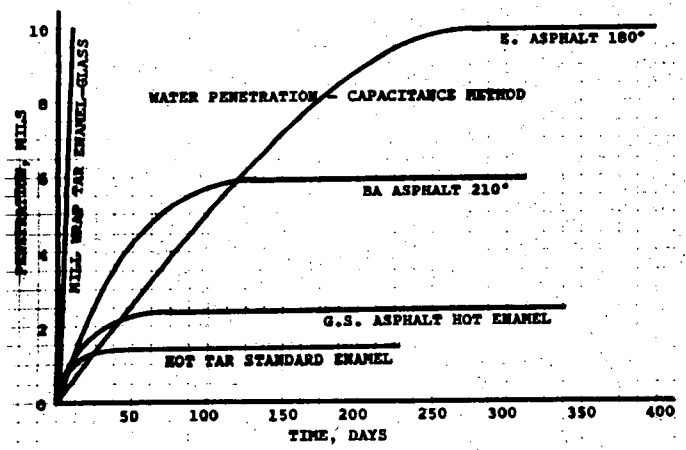

Fig. 11

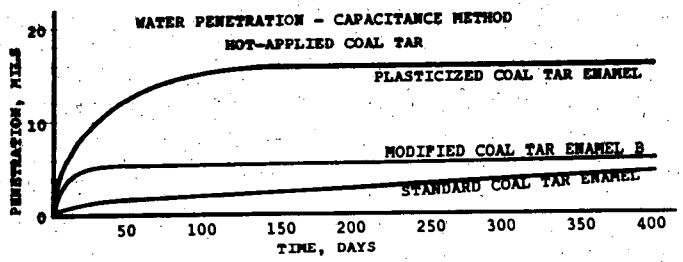

Fig. 13

WATER PENETRATION - CAPACITANCE METHOD

400 DAYS - 70°F WATER - VOLUME RESISTIVITY 70000 OHMS

TYPE	t (MILS)	(K)	t_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)	51	6.34	2.00	over 10^{14}
ASPHALT OXIDIZED ALIPHATIC 230°F (HOT-APPLIED)	36	5.55	1.50	over 10^{14}
ASPHALT H 220°F (HOT-APPLIED)	95	6.68	1.50	over 10^{14}
COAL TAR PLASTICIZED ENAMEL AWWA (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 PLASTICIZED 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 K 220°F (HOT-APPLIED)	86	7.25	2.30	over 10^{14}
ASPHALT H2 220°F (HOT-APPLIED)	113	8.70	2.60	over 10^{14}
ASPHALT E 220°F (HOT-APPLIED)	65	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

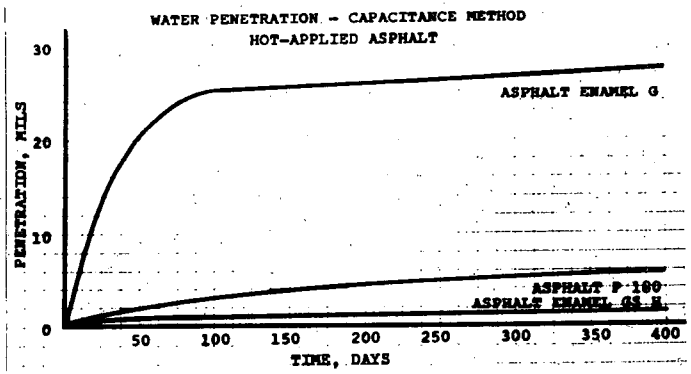

Fig. 14

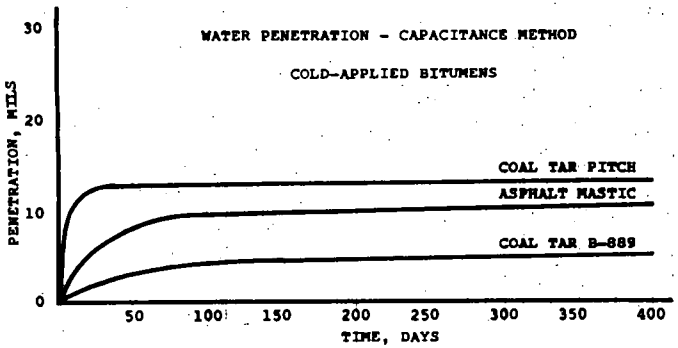

Fig. 15

WATER ABSORPTION - GRAVIMETRIC
AND
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	t' (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

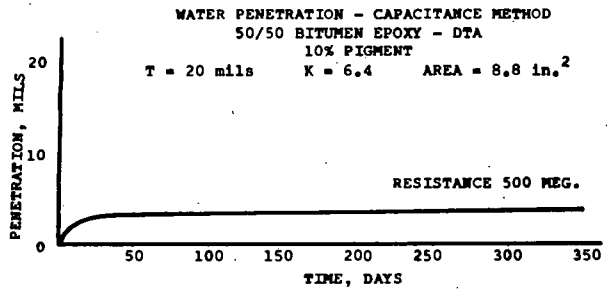

Fig. 16

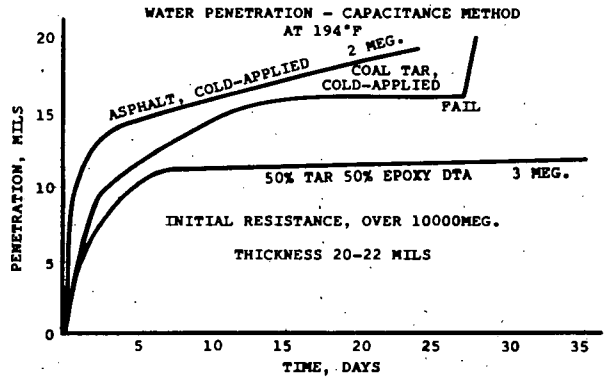

Fig. 18

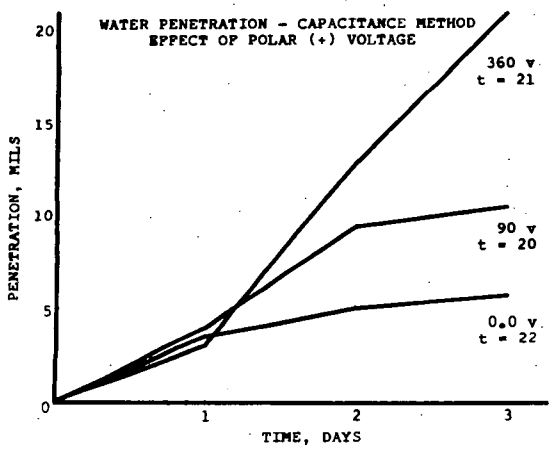

Fig. 19

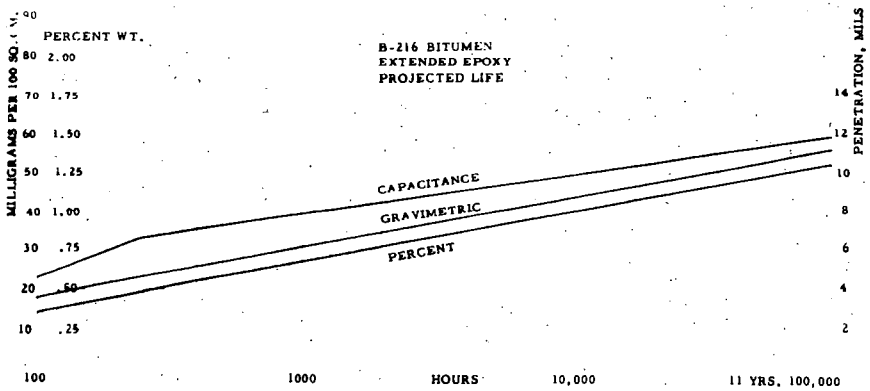

Fig. 21

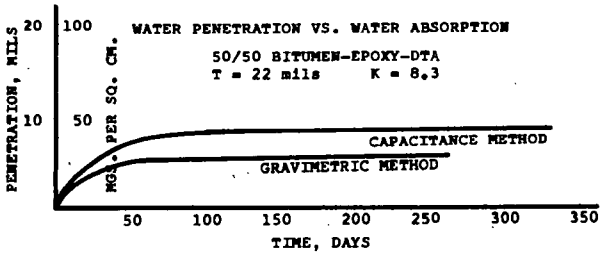

Fig. 20

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.

	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

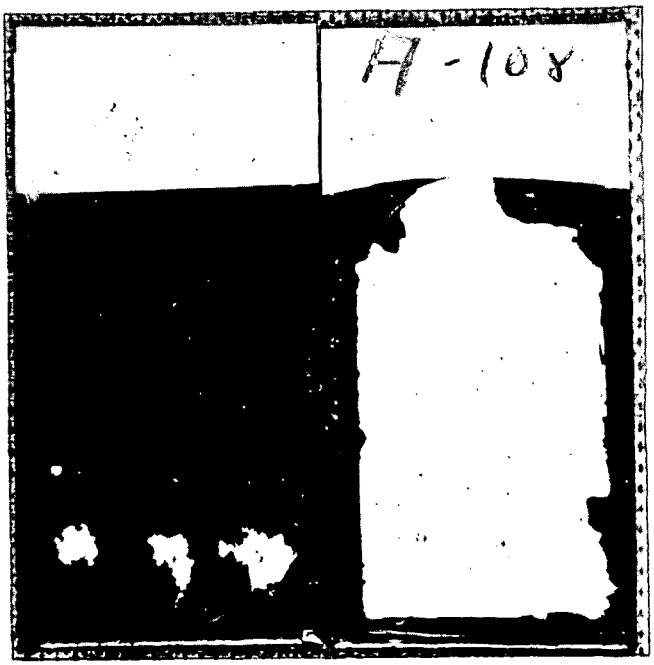

Fig. 24

Fig. 25

Fig. 26

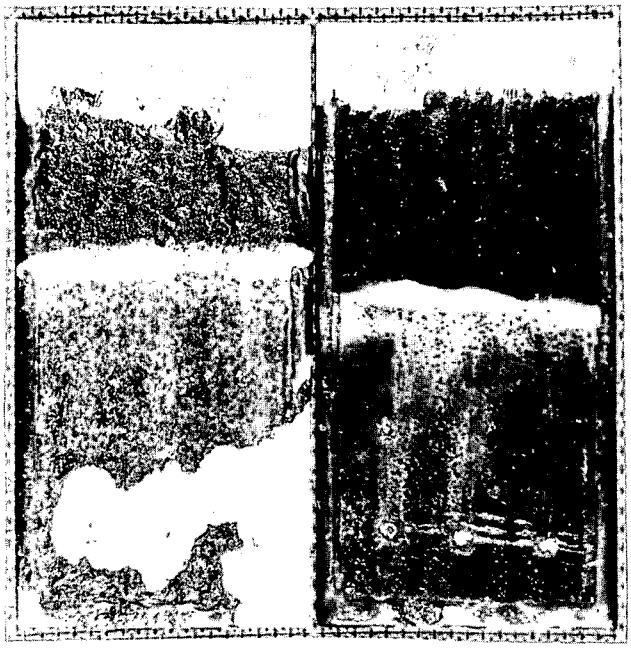

Fig. 27

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 absorbence 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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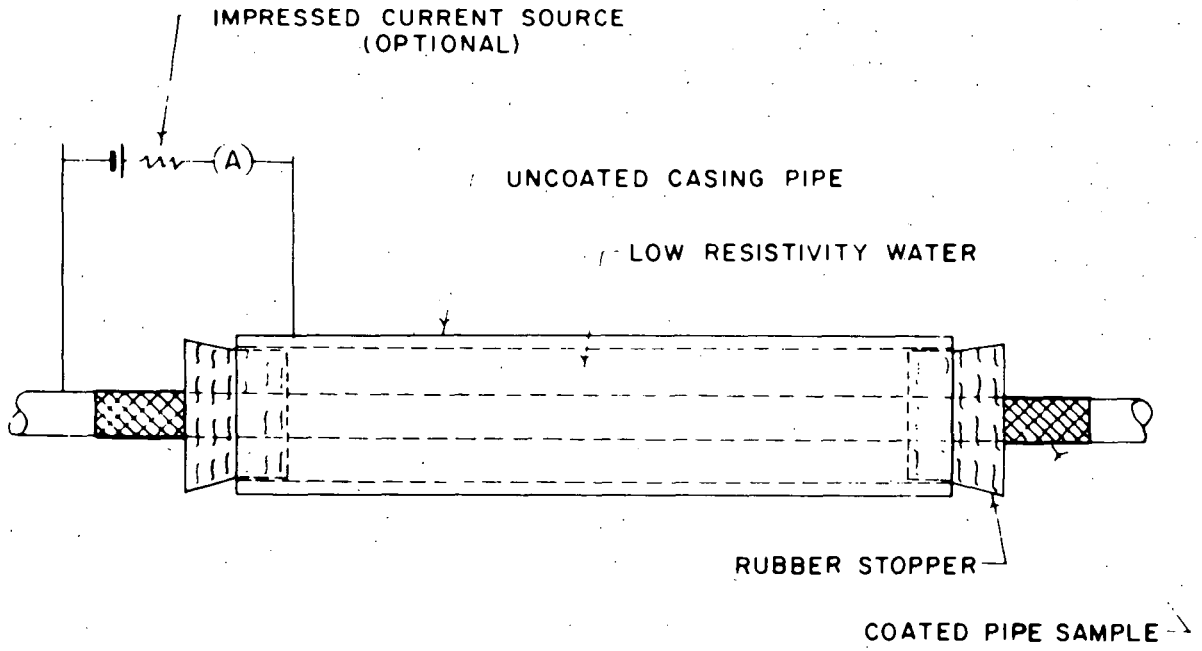
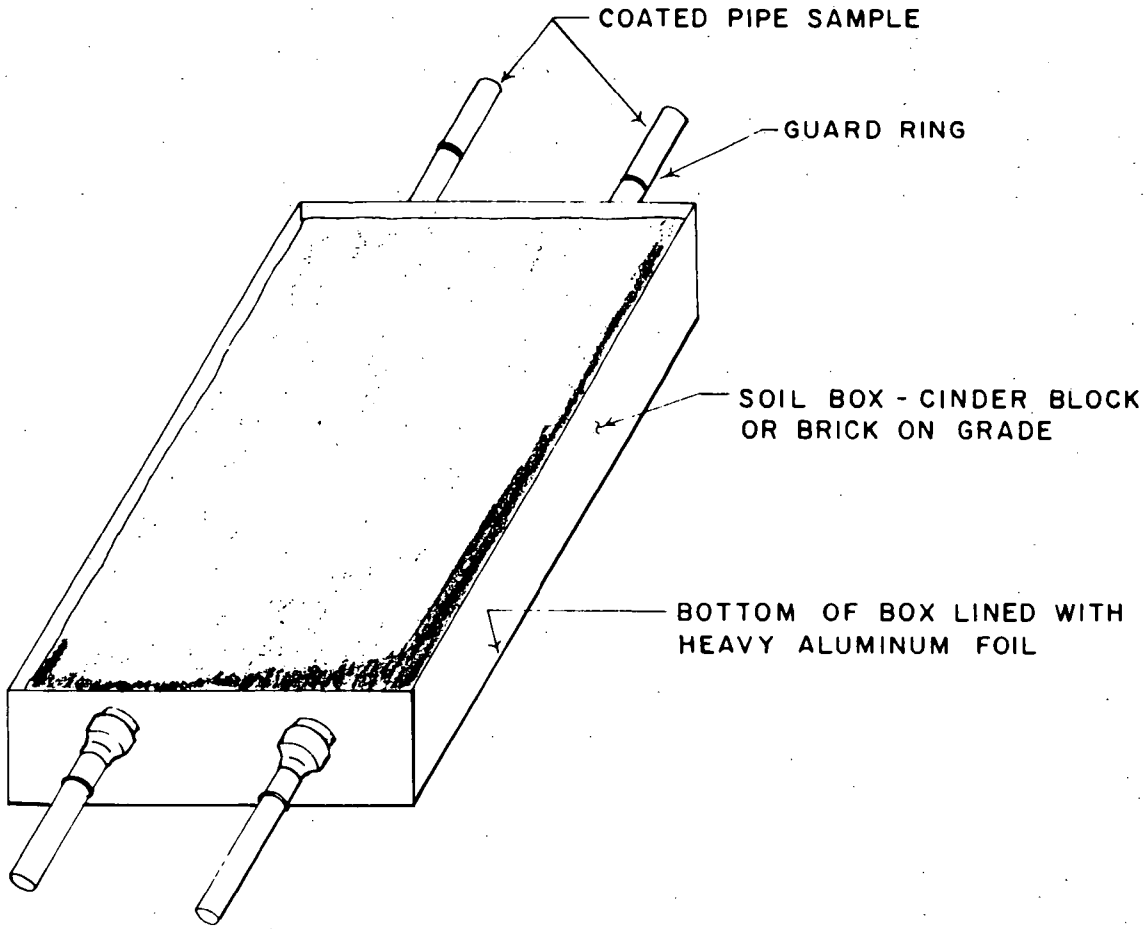


MODIFIED SALT-CROCK TEST

FIGURE 1



CONTROLLED SOIL ENVIRONMENT TEST

FIGURE 2

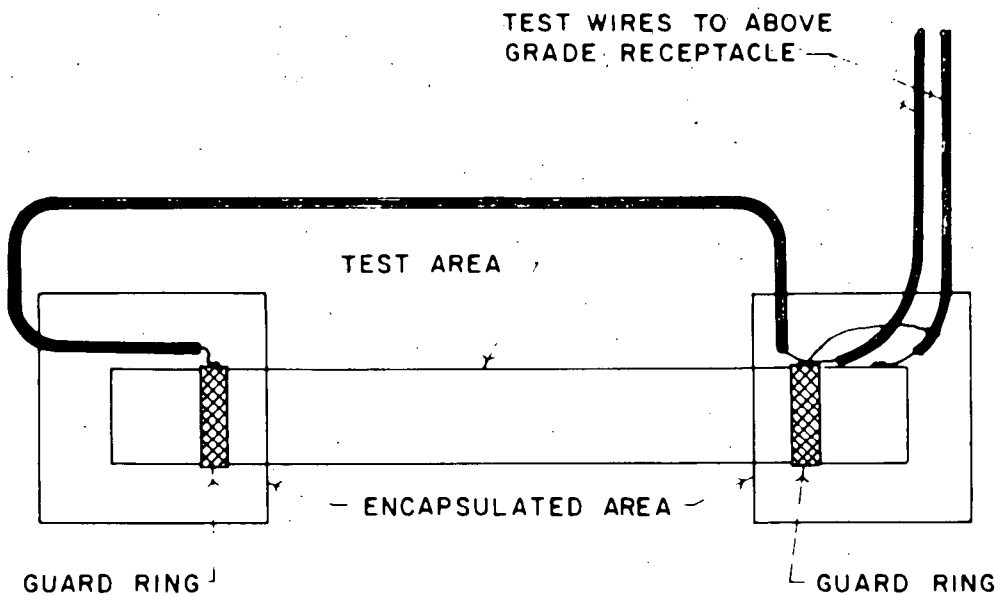

TEST WIRES TO ABOVE
GRADE RECEPTACLE
TEST AREA
ENCAPSULATED AREA
GUARD RING
GUARD RING

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 nonconductor 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 diagramatically 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 predetermined 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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(2) Harris, J. O., "Microbiological Studies Reveal Significant Factors in Oil and Gas Pipeline Back-Filled Ditches", Kansas State University Technical Bulletin 135, December, 1963.

(3) Harris, J. O., "Microbiological Studies Reveal Significant Factors in Oil and Gas Pipeline Back-Filled Ditches", Kansas State University Technical Bulletin 102, May 20, 1959.

(4) American Water Works Association, "A.W.W.A. Standard for Coal Tar Enamel Protective Coatings for Steel Water Pipes", C203-62.

(5) National Bureau of Standards, "Underground Corrosion", Circular 579.

(6) American Society for Testing Materials, "Test for Water in Bituminous Materials", ASTM D-95.

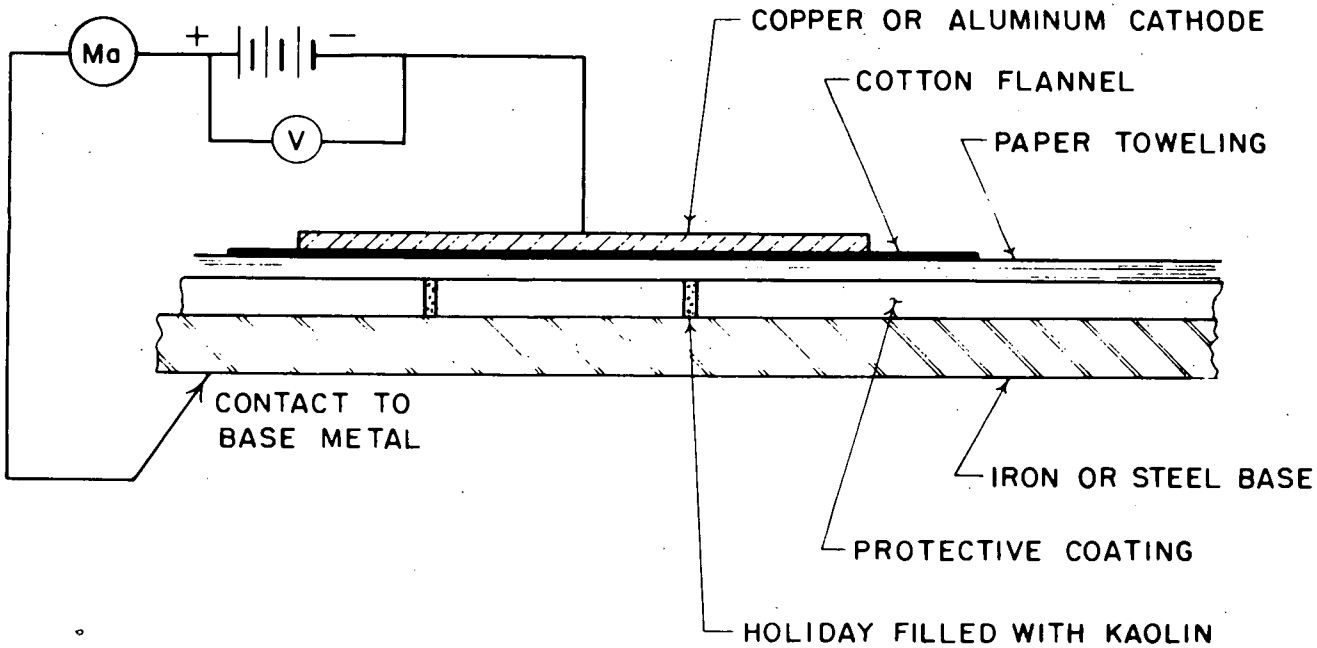
(7) Traxler, R. W., "Microbiological Degradation of Asphalt", American Chemical Society, 142nd National Meeting, Atlantic City, September, 1962.

(8) Killam, E. T. et al, "Report of Committee on Pipe Line Friction", Journal of New England Water Works Association, Vol. XLIX No. 3, pp 235 to 342.

(9) National Association of Corrosion Engineers Technical Committee T-3D Report, "Methods for Measuring Leakage Conductance of Coating on Buried or Submerged Pipe Lines". "Corrosion" Vol. 13, 1957, pp 803t - 805t.

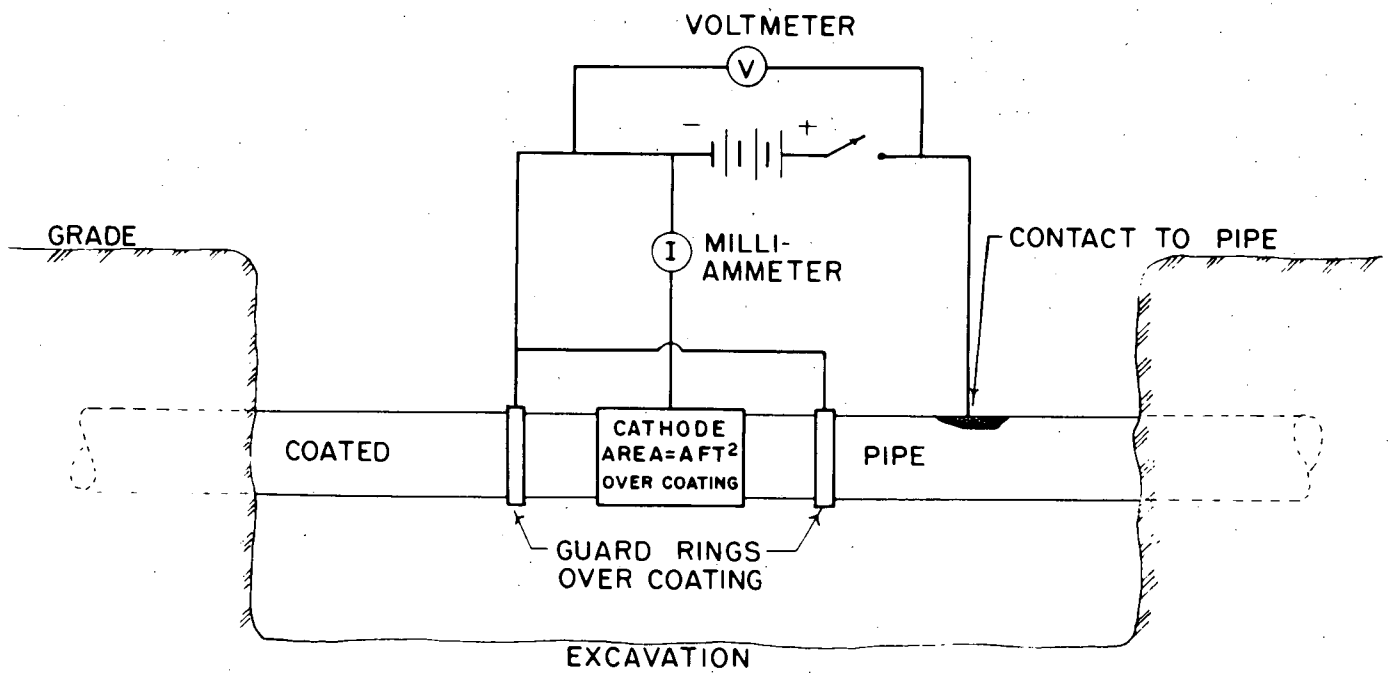
(10) Schwertfeger, W. J., "Corrosion Rates of Ferrous Alloys (Fe - Cr and Fe - Cr - Si) Measured by Polarization Techniques". "Corrosion" Vol. 19, 1963, pp 17t - 25t.

(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

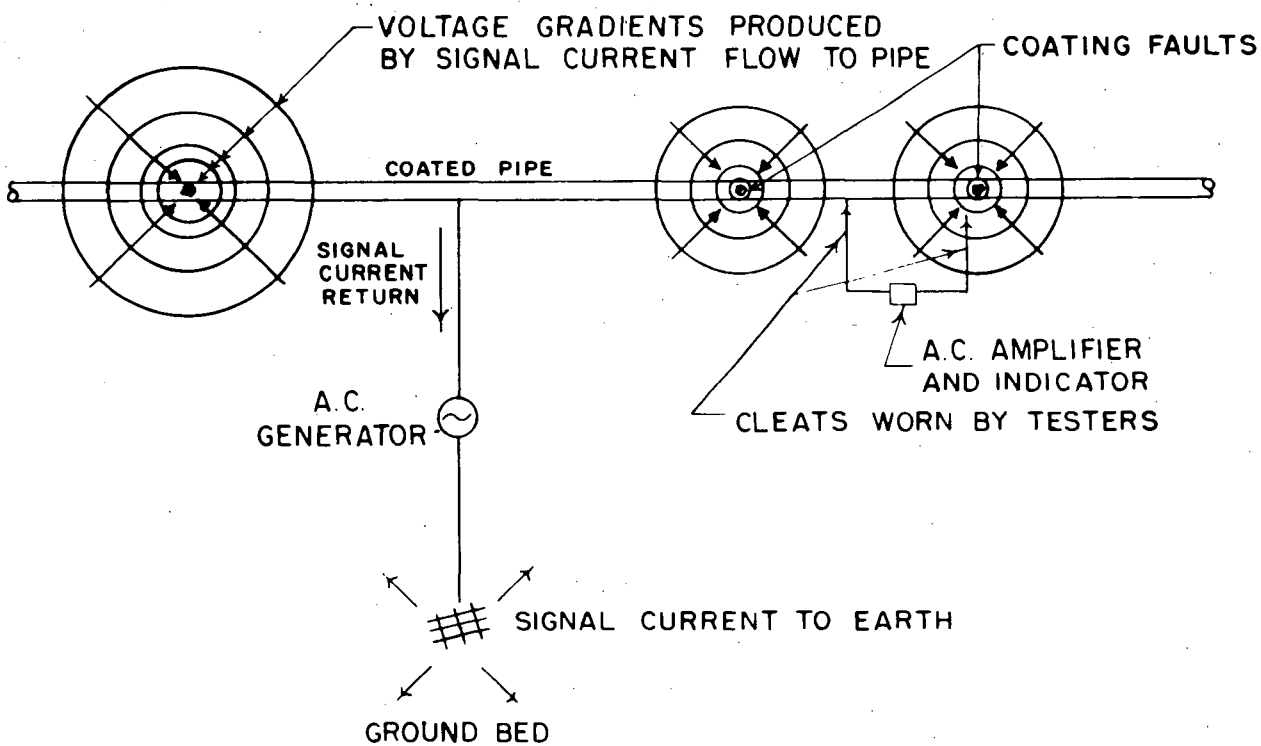
FIGURE 1



$$\text{COATING CONDUCTANCE} = \frac{\Delta I}{\Delta V} \times \frac{1}{A} \text{ mhos/FT}^2$$

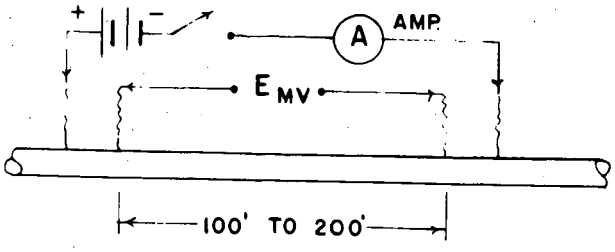
CONDUCTANCE MEASUREMENTS

FIGURE 2



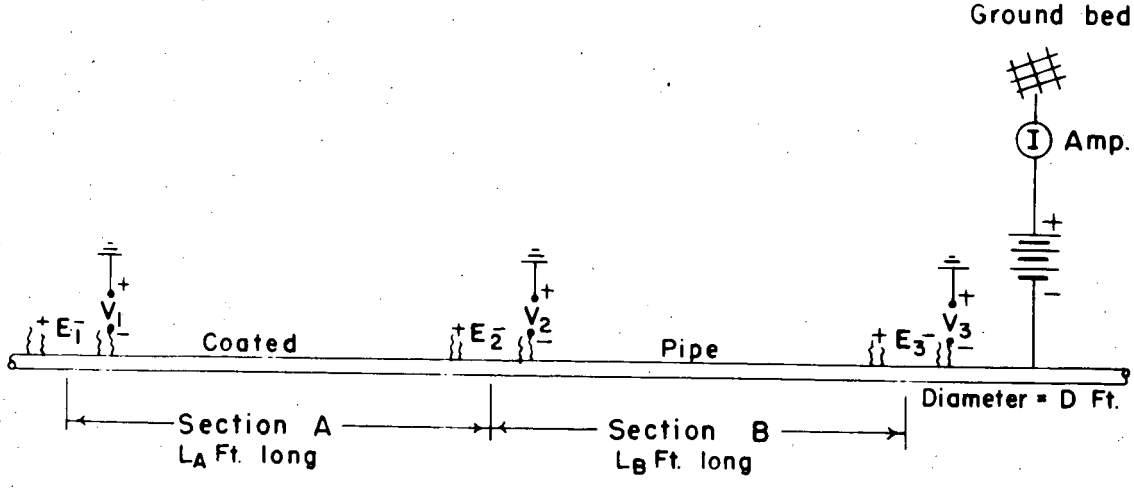
PEARSON COATING FAULT DETECTOR

FIGURE 3



$$\text{Factor} = \frac{\Delta A}{\Delta E} \text{ AMPS/ M.V.} = K$$

CALIBRATION SET UP



$$\text{Average Conductance, Section A} = \frac{\Delta E_2 \times K_2 - \Delta E_1 \times K_1}{\Delta I} \times \frac{2\Delta I}{\Delta V_1 + \Delta V_2} \times \frac{1}{\pi \times D \times L_A}$$

$$= \frac{\text{mhos}}{\text{FT}^2}$$

FIGURE 4

FIGURE 5

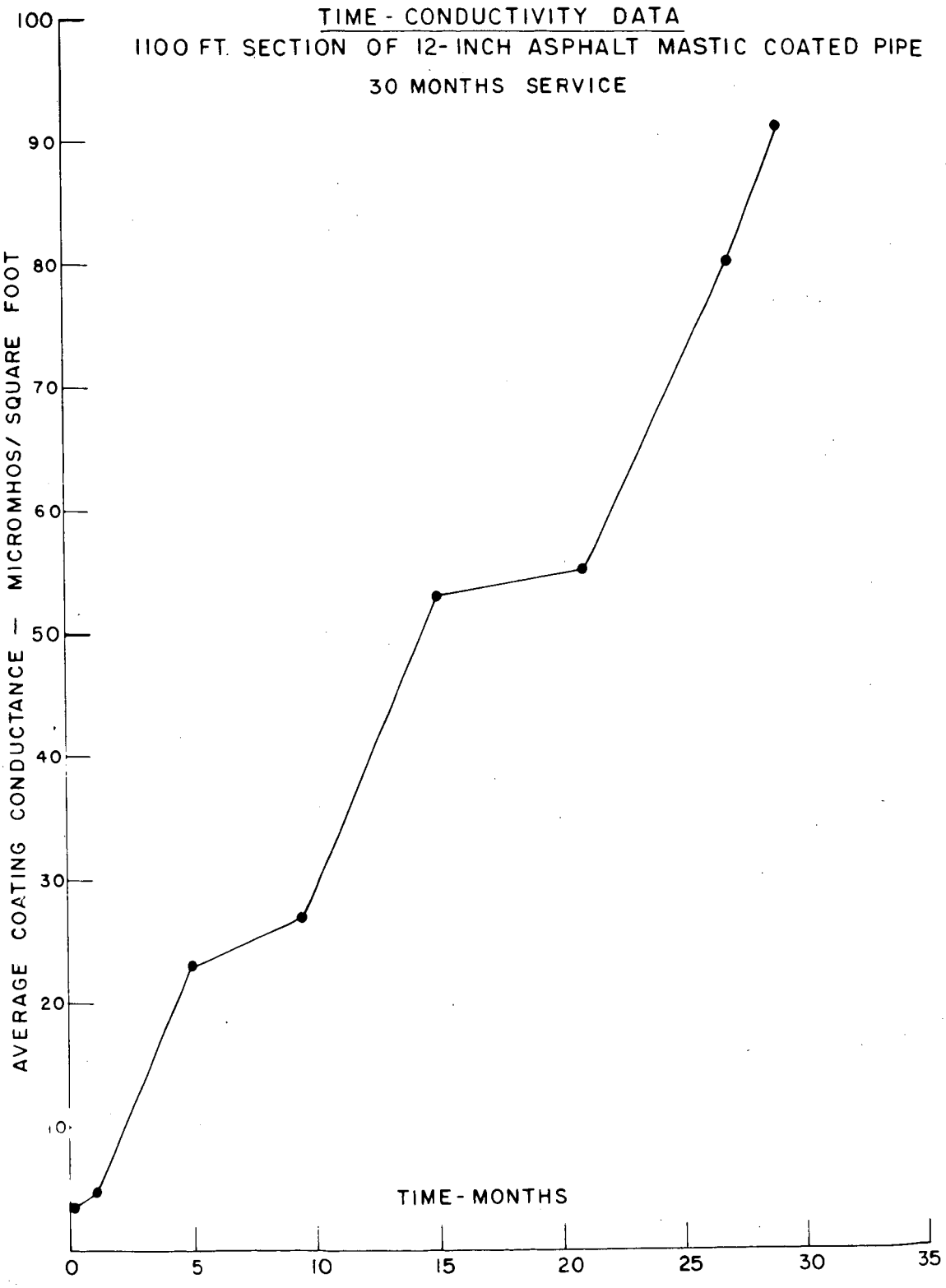
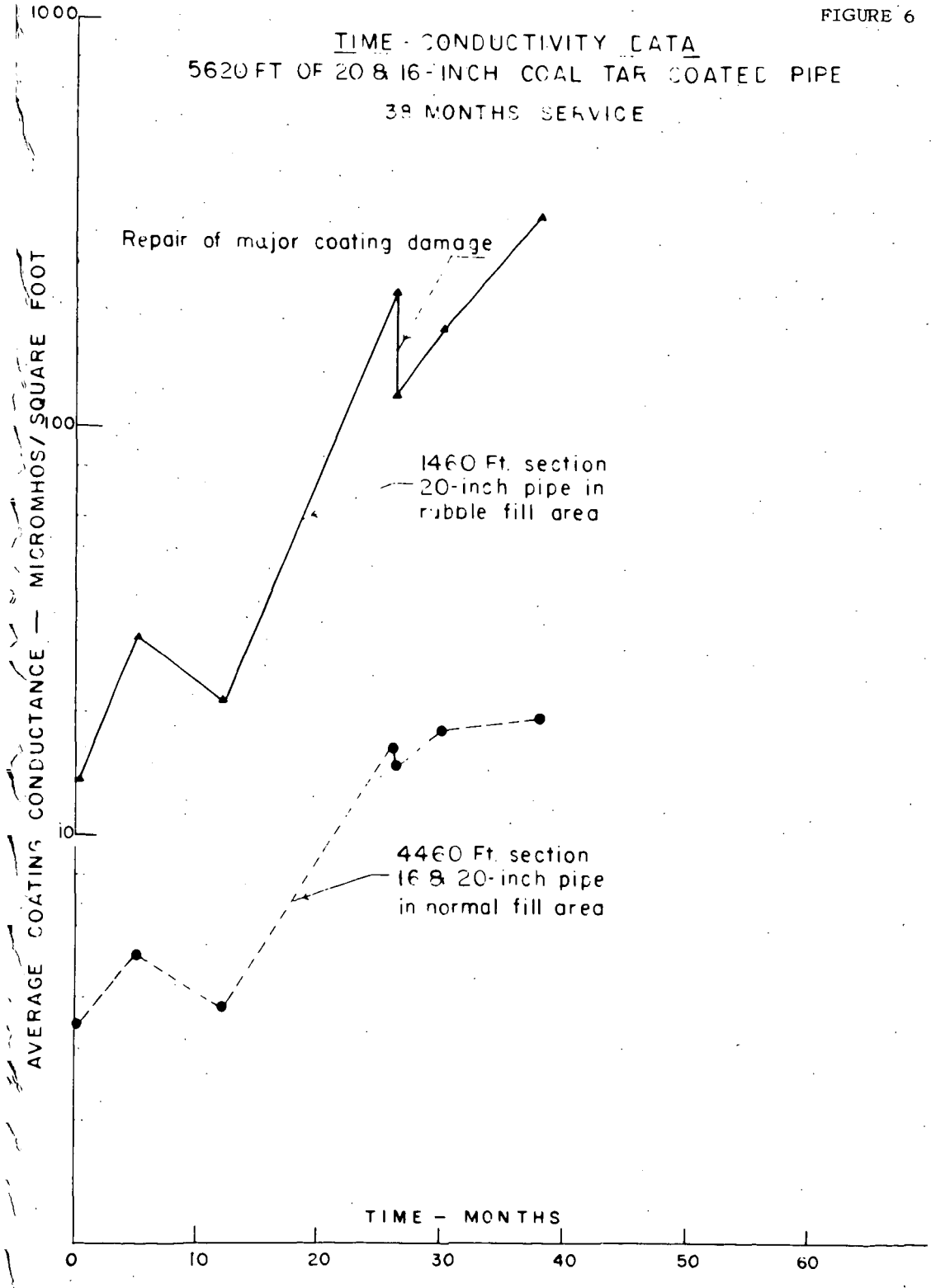

TIME - CONDUCTIVITY DATA
1100 FT. SECTION OF 12-INCH ASPHALT MASTIC COATED PIPE
30 MONTHS SERVICE
AVERAGE COATING CONDUCTANCE - MICROMHOS/ SQUARE FOOT
100
90
80
70
60
50
40
30
20
10
TIME - MONTHS
0
5
10
15
20
25
30
35

FIGURE 6


TIME - CONDUCTIVITY DATA
5620 FT OF 20 & 16-INCH COAL TAR COATED PIPE
38 MONTHS SERVICE
Repair of major coating damage
1460 Ft. section
20-inch pipe in
rubble fill area
4460 Ft. section
16 & 20-inch pipe
in normal fill area
AVERAGE COATING CONDUCTANCE — MICROMHOS/SQUARE FOOT
1000
100
10
TIME — MONTHS
0
10
20
30
40
50
60

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.

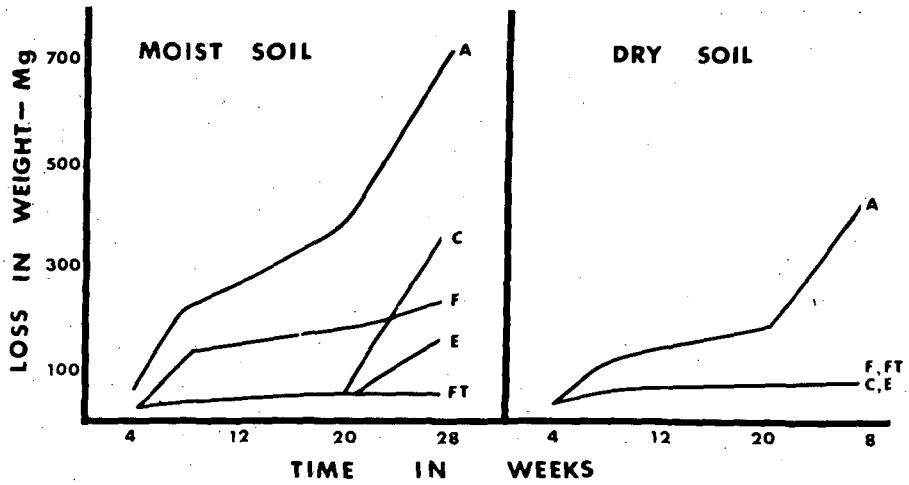


FIG. 1:--EFFECT OF SOIL BURIAL ON WEIGHT LOSS OF BITUMEN COATED TONGUE BLADES.

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 °F	SPECIFIC GRAVITY 77°F	PENETRATION 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

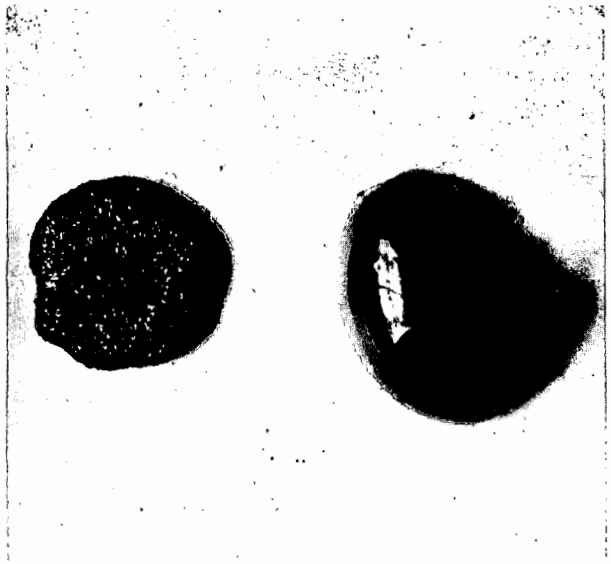


FIG. 3:--ASPHALT SAMPLES COLLECTED FROM CULTURE FLASKS. TEST FLASK ON LEFT, CONTROL FLASK ON RIGHT.

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.

ASPHALT	RELATIVE VISCOSITY*	
	M. ranae	N. coeliaca
1A	2.0	1.4
3A	3.3	3.8
6A	-	6.8

$$*\text{RELATIVE VISCOSITY} = \frac{\text{VISCOSITY DEGRADED ASPHALT}}{\text{VISCOSITY CONTROL ASPHALT}}$$

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	*Ps.* 196Aa	*M. ranae*	*N. coeliaca*
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.

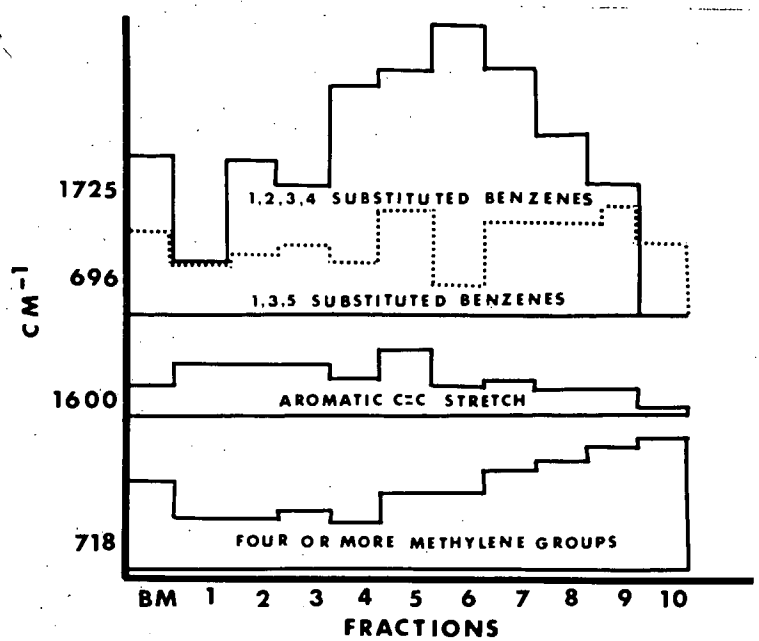
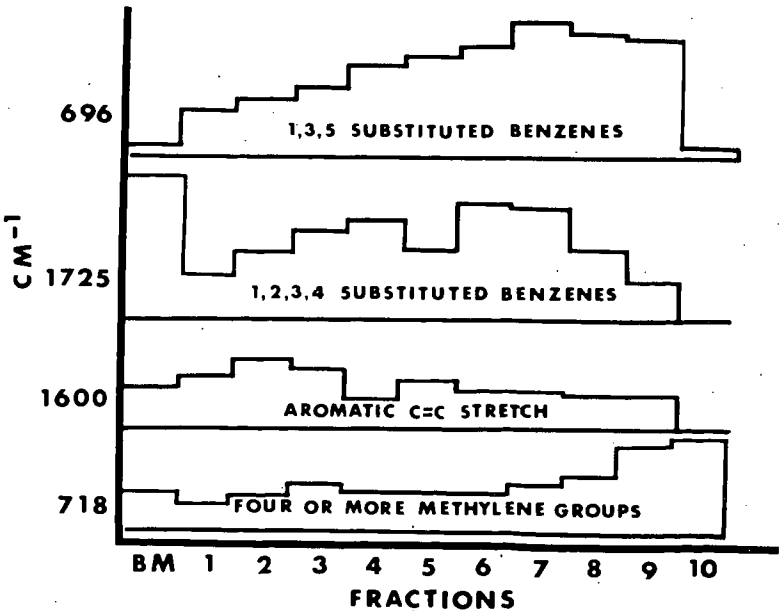


FIG. 4:--

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.



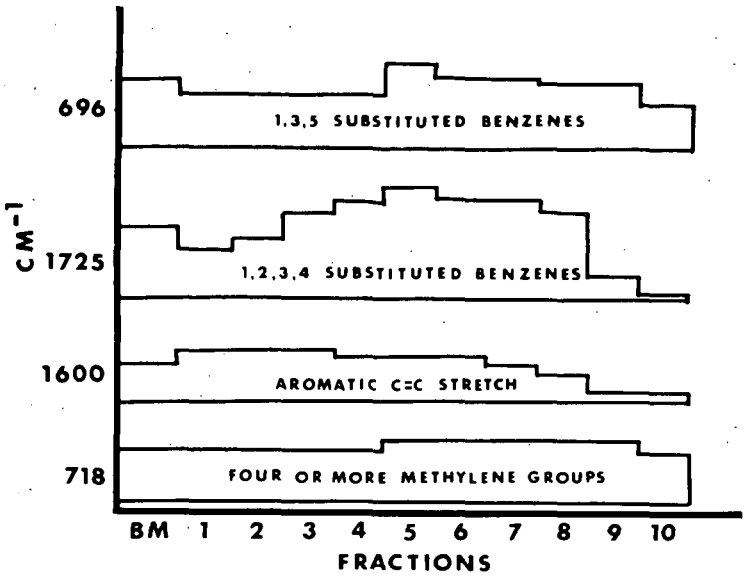


FIG. 6:--INFRARED SPECTRA OF BASE MATERIAL AND THERMAL DIFFUSION FRACTIONS FROM ASPHALT 6A.

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*	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		FATTY ACIDS	
LEXANE	175	LEXANOIC	75
LEPTANE	195	LEPTANOIC	105
OCTANE	200	OCTANOIC	115
NONANE	229	NONANOIC	100
DECANE	200	DECANOIC	95
DODECANE	220	DODECANOIC	183
TRIDECANE	230	-	
TETRADECANE	260	TETRADECANOIC	180
HEXADECANE	260	HEXADECANOIC	190
OCTADECANE	200	OCTADECANOIC	260
EICOSANE	250	-	
DOCOSANE	220	BEHENIC	0
ALKENES		**AROMATIC**	
1-HEPTENE	0	BENZENE	0
1-OCTENE	210	ETHYLBENZENE	0
1-DECENE	178	PROPYLBENZENE	0
1-DODECENE	120	TRIMETHYLBENZENE	0
1-TETRADECENE	300	PENTAMETHYLBENZENE	0
1-HEXADECENE	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% PROPYLBENZENE	110	170
1.0% PROPYLBENZENE	5	15
2.0% PROPYLBENZENE	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	MAXIMUM TURBIDITY										
	BM*	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.

TABLE VIII

SUBSTRATE SPECIFICITY OF *Mycobacterium ranae*.

n-ALKANES		FATTY ACIDS	
HEPTANE	0	HEPTANOIC	5
OCTANE	0	OCTANOIC	5
DECANE	0	DECANOIC	5
DODECANE	55	DODECANOIC	80
TRIDECANE	60	-	
TETRADECANE	60	TETRADECANOIC	125
HEXADECANE	60	HEXADECANOIC	65
OCTADECANE	60	OCTADECANOIC	170
EICOSANE	125	-	
DOCOSANE	75	BEHENIC	40
ALKENES		**AROMATIC**	
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

THIS WORK WAS SUPPORTED IN PART BY GRANT 907-A2 FROM THE PETROLEUM RESEARCH FUND OF THE AMERICAN CHEMICAL SOCIETY. THE AUTHOR ALSO WISHES TO EXPRESS APPRECIATION TO R. N. TRAXLER, TEXAS TRANSPORTATION INSTITUTE FOR THE ASPHALTS AND ASPHALT FRACTIONS USED IN THIS INVESTIGATION, AND FOR THE INFRARED DATA ON THE THERMAL DIFFUSION FRACTIONS.

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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 COMMERCIALLY-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.

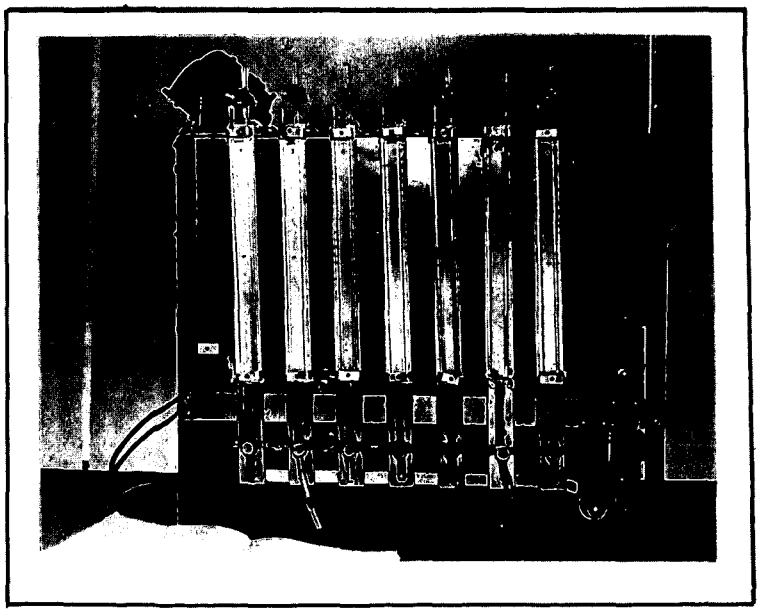

Fig. 1:--The Warburg microrespirometer shown here was used to show rapid oxidation of hydrocarbons by normal soil microorganisms.

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

SOIL	TOTAL BACTERIA (MILLIONS/GM/SOIL)	ACTINOMYCETES (MILLIONS/GM)	FUNGI (THOUSANDS)	HYDROCARBON BACTERIA (PER GRAM)
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	PASTURE SOIL		WHEAT FIELD		GARDEN SOIL	
	BACTERIA (M)	HC TYPES (T)	BACTERIA (M)	HC TYPES (T)	BACTERIA (M)	HC TYPES (T)
	PER GRAM		PER GRAM		PER GRAM	
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.

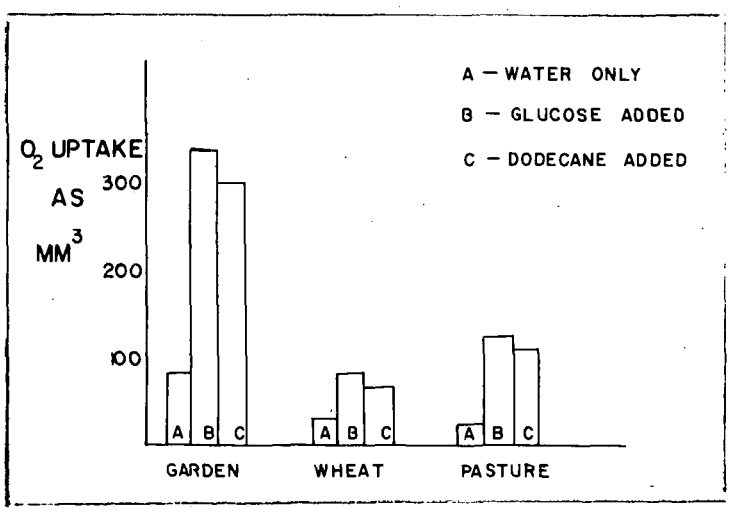

Fig. 2:--One per cent glucose, dodecane, or only water was added to normal soils. Total respiration as mm^3 in six-hours interval shows dodecane readily oxidized by the normal soil population.

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

HYDROCARBON BACTERIA PER GRAM OF SOIL	UNDISTURBED SOIL IN RIGHT-OF-WAY AT PIPELINE DEPTH	SOIL ADJACENT TO ASPHALT COATING
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					
Aerobes	Anaerobes	Aerobes	Anaerobes	Sample No. 1	Sample No 2		
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.

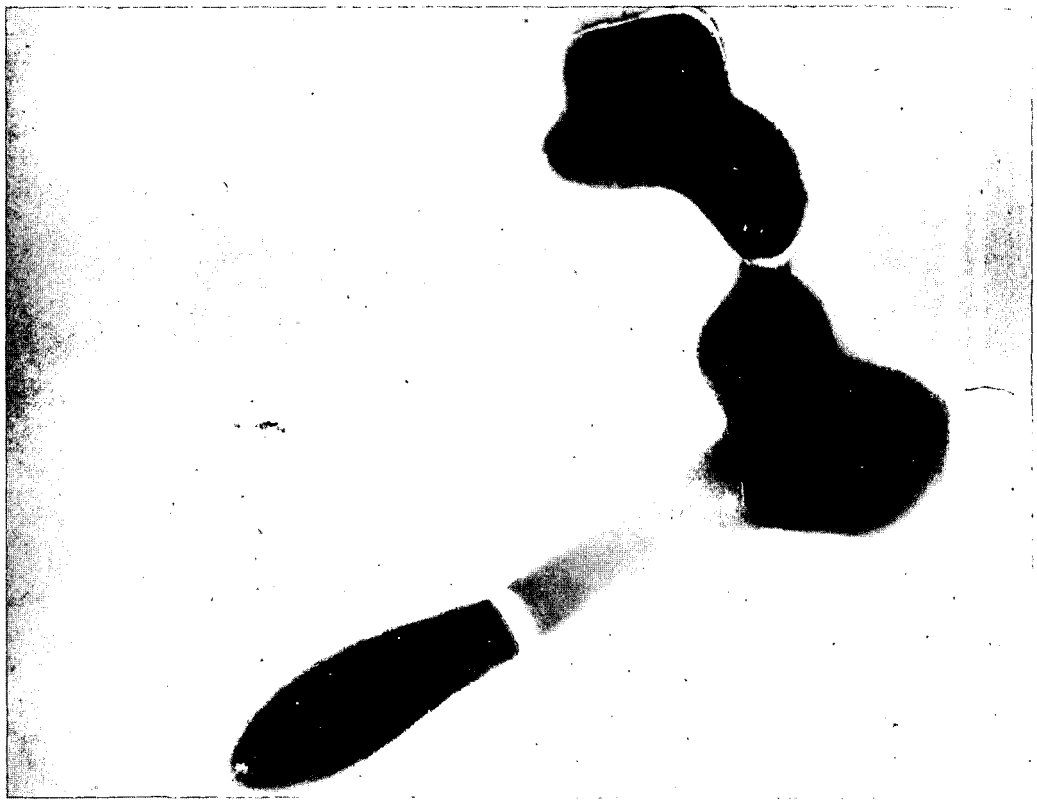

Fig. 3:--53,200 magnification. *Pleomorphic* rod-shaped cells, commonly seen in species of *Nocardia*, a common type of actinomycete isolated from asphalt coatings. Moisture under the coating -- some pitting -- anaerobic corrosion on the pipe -- no bond of coating -- 10 years' underground service. In 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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