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PROPERTIES AND REACTIONS EXHIBITED BY ANTHRACITE LITHOTYPES UNDER THERMAL STRESS

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Although anthracite is no longer as important a metallurgical fuel as formerly, its chemical and physical properties as well as the advantageous location of the anthracite fields make consideration of its use as a metallurgical fuel imperative. Attempts to use raw anthracite as a fuel for blast furnace and cupola operations have shown it to be less satisfactory than coke. The major limitation in the use of anthracite in the metallurgical industry is its tendency to decrepitate when subjected to extreme temperature gradients. The extent of this decrepitation varies depending upon the heating conditions and the nature of the coal. The decrepitation of anthracite, when subjected to thermal shock, is believed to be caused by several factors including rapid moisture and volatile matter evolution, crystallite growth and differential expansion of anthracite laminations (see Delvaux et al, 1957, Eckerd et al, 1957, and Nelson et al, 1958). Decrepitation is the occurrence of one or a combination of these factors resulting in an internal pressure in excess of that required to overcome the physical strength of the material. The thermal decrepitation, then, is a disintegration of the anthracite when subjected to high temperatures which cause excessive pressure drops during cupola and blast furnace operation resulting in restricted gas and air flow in the stock column. The decrepitation process of anthracite is the total effect resulting from a series of reactions which are dependent upon the physical and chemical properties of the coal, and one grain of anthracite may or may not produce a product of physical strength comparable to another under identical thermal conditions.

An informative review of previous work in this field (Nelson et al, 1958) shows that investigation of anthracite decrepitation has been concerned primarily with the treating of lump coal. However, it is felt that disruption of equal importance occurs when small size particles are involved. This is of significance because of the possible effect of such fracturing on the strength of a metallurgical coke produced with anthracite in the blend. Thus, an investigation was undertaken to determine the behavior of petrographically distinct anthracite particles under thermal stress.

Equipment and Methods of Investigation

To adequately study the decrepitation phenomena of small particles a Leitz 0-1000°C. heating stage was employed. This stage was mounted on a Leitz Panphot microscope which is equipped with optics to allow observation with oblique illumination at 28.5 to 137.5 diameters. Vertical illumination is possible in the 42x to 562.5x range. The objectives giving the first range are most often employed because of their long working distance and therefore they are safer from any deleterious effects of high temperatures. The rate of heating is controlled manually and temperatures are read directly on a "direct-reading" galvanometer. The instrument as used is shown in Plate I. A close-up of the microfurnace is shown as Plate II. A grain of anthracite can be seen in place, through an open window, on a quartz specimen holder. Preliminary examination of anthracite particles showed that all coals studied could be readily shown to consist of four types of particles. These are: 1) a bright particle, having a vitreous luster and exhibiting conchoidal fracture; 2) a dull particle with a matte surface and irregular fracture; 3) a mixture of one and two as more or less alternating bands; and 4) grains having a fibrous, porous structure and appearing like charcoal. For these four lithotypes the terms vitrain, durain, clarain and fusain have been tentatively employed. Representative grain types are shown on Plate III.

The materials selected for study were taken from the plus 2 inch fraction of channel samples. The seams represented are the middle split of the Mammoth Seam and the Primrose Seam, both from Northumberland County, Pennsylvania, and the Buck Mountain Seam from Schuykill County, Pennsylvania. In the order presented they are referred to as anthracites A, B and C.

Two particle sizes were selected for study, 10 x 14 mesh and 6 x 10 mesh. The anthracites were subjected to the following experimental conditions: 1) gradual heating to temperatures ranging from 500°C. to approximately 1000°C. at varying heating rates; 2) shock heating at temperatures ranging from 300°C. to approximately 1000°C. for varying times and with different particle sizes; and 3) preheating to varying temperatures prior to shock heating.

Effect of Heating Rate on Decrepitation

Investigations were carried out concerning the effect of heating rate on decrepitation. Table 1 shows the relation between the temperature at which decrepitation first visibly occurred and the heating rate. In the absence of a program controller heating rates less than 5°C. per minute were not accurately attainable. These experiments were performed with clarain grains. The maximum temperatures employed were in the range of 920°C. to 960°C. These figures show no significant relation between heating rate and observable decrepitation, although at the higher heating rates the decrepitation did consistently occur initially at a higher temperature.

Table 1

Effect of Heating Rate on the Temperature at Which Decrepitation First Visibly Occurred[1]

Heating Rate (°C./min.)	Temperature at Which Visible Decrepitation First Occurred (°C.)
5	750
10	800
15	600
20	650
40	675
50	800
57	800
70	800
78	(after cooling)

[1] Experiments carried out on the +2" fraction of "Anthracite B"

Most of the work done on the effect of gradual heating was with clarain particles because the other petrographic entities of the anthracite used, vitrain, durain, and fusain, underwent no visible decrepitation whatever when subjected to heating rates varying from 25°C. per minute to 63°C. per minute to maximum temperatures of 940°C. to 980°C. However, while no decrepitation in fusain particles was observed, these particles after treatment were much weaker than before and were very easily crushed.

An attempt was made to correlate change in weight of the particles due to heating with thermal decrepitation. The existence of such a relationship seems reasonable in view of the believed causes of decrepitation, in particular rapid evolution of moisture and volatile matter. These experiments were carried out with clarain particles of "Anthracite B" subjected to heating rates of 5°C. per minute to 78°C. per minute. Figure 1 shows no definite relation between weight change due to heating and heating rate, either with or without segregation according to range of particle size, although a general decrease in weight loss occurs for increasing heating rates.

A general decrease in friability at low heating rates is in accord with prior investigations (Grace and Jackson, 1954; Jackson and Grace, 1954; Geller et al, 1955) which reasoned that lower heating rates permit sufficient time for the gases to escape without developing critical gas pressures within the coal structure greater than those sufficient to overcome the physical strength of the material. Recent work (Delvaux et al, 1957) has reported an initial rise in friability at low heating rates.

Effect of Shock Heat on Decrepitation

The different petrographic entities studied were subjected to shock heat treatment at temperatures varying from 500°C. to 970°C., the time of shock heat varying from 10 to 15 minutes. Table 2 and Plate IV show the results of this work. Durain and vitrain first demonstrated observable decrepitation when subjected to shock heat at 950°C. Although fusain showed no visible cracking until shock heat at 950°C., the treated product in each case of shock heat at lower temperatures was so powdery and easily crushed that it was concluded that decrepitation had occurred to a great extent. Clarain was the only entity to undergo visible decrepitation at a shock heat temperature below 950°C., doing so at 800°C. The decrepitation which clarain underwent was more immediate and more violent than that of the other entities.

Table 2

Effect of Shock Heat on Visible Decrepitation[1]

Temperature of Shock Heat °C.	Vitrain	Durain	Fusain	Clarain
500	None Visible	None visible	No visible cracking occurred but treated product easily crushed	None visible
600	None visible	None visible	" "	None visible
700	None visible	None visible	" "	None visible
800	None visible	None visible	" "	Grain split in half immediately on placing in furnace
950	Visible cracking and splitting of grain	Visible cracking	Visible cracking	Immediate cracking and splitting occurred

[1]Experiments carried out on the +2" fraction of "Anthracite B"

Plate IV shows petrographic particles before any treatment and the resulting products after subjection to shock heat at various temperatures. These particles were all shock heated for 10 to 15 minutes in a nitrogen atmosphere.

Clarain was selected for more detailed study under thermal shock conditions on the basis of the results presented in the preceeding paragraphs which indicate a more observable decrepitation present in these than in the other particles. Clarain particles within a weight range of 1 to 8 milligrams from Anthracites A, B and C were subjected to shock heat treatment. Figure 2 shows the relation between loss of weight and shock heat temperature. For each series of experiments except Anthracite B(2) the critical temperature (the temperature above which further increases in shock heat temperature produce a significant increase in decrepitation) is in the range of 625°C. to 675°C. Anthracites A and B underwent visible decrepitation in all but a very few experiments on shock heating at 700°C. or greater, while Anthracite A showed almost no observable cracking even at 900°C. At the higher temperatures of shock heat (700°C. and above) there was a tendency for the light vitrain bands to blend into and become indistinguishable from the dull durain background.

Experiments were run varying the time of shock heat in an attempt to determine whether decrepitation is primarily an immediate phenomenon or one dependent upon time of exposure to heat. While the degree to which a given anthracite will fragment or decrepitate varies depending on the heating conditions and the nature of the coal, clarain particles of "Anthracite B" were chosen because of their tendency to readily undergo decrepitation. Although there is a general disparity of results as shown by Figure 3, the trend shows that at the shock heat temperature employed, 800°C., decrepitation as related to the weight loss is not an entirely immediate effect. Many of the experiments shown in Figure 3 resulted in cracking immediately on placing the clarain grain in the furnace at 800°C., but in several cases no cracks were visible until the entire heating period was completed.

A likely source of the wide difference of percent weight loss in Figure 3 (in particular at 10, 15 and 25 minutes) as well as in the other weight loss calculations is the necessity of working with very small quantities, of the order of 1.5 to 15 milligrams, from which it follows that a difference in weight of 2/10 of one milligram can cause a difference in weight lost of from 13 percent down to 1 percent, depending on the size of the particle examined.

Effect of Particle Size on Decrepitation

As considerable work had been done in the past on the effect of size of anthracite on decrepitation, an investigation was made into the relation between particle size and thermal decrepitation for each of the petrographic entities being studied. Figures 4 and 5 show the relation between loss in weight due to heating and the original particle weight. Although the amount of weight lost increased in each case with the particle size (Figure 4), the percent loss (Figure 5), with the exception of durain, either remained nearly the same or decreased with increasing particle size. These results are contrary to evidence reported by previous workers (Wright et al, 1941; Delvaux et al, 1957; Eckerd and Tenney, 1957; Anthracite Institute) who found that the degree of decrepitation increases with the size of the coal. There are two relevant distinctions between the past work and that carried out in the instant investigation: 1) all past work was performed with lump size coal while this investigation dealt solely with much smaller sized particles; 2) the previous studies were of anthracite as "whole coal", while this work was concerned with the petrographically distinct entities of anthracite.

A concept often used to explain the increased decrepitation of larger sized anthracite is that the increased surface area indicates a less dense structure and hence lesser strength. This would seem to have a minimum of applicability here where, though increased particle size is accompanied by increased surface area, the sizes of all the particles are so small as to render any difference in decrepitation due solely to particle size nominal.

The study of anthracite decrepitation on a petrographic basis causes another distinction to be made. For a given anthracite, though two or even three of the four petrographic entities may show either no change or even a decrease in decrepitation for increased particle size, an increase in decrepitation which the other entity may undergo could be more than sufficient to offset the total decrease of the other entities and cause the anthracite to suffer a net increase in decrepitation with increased particle size. Due to the heterogeneous nature of coal, the decrepitation characteristics of one anthracite need have no necessary relation to those of another anthracite (Figure 2).

This investigation does not purport to show that decrepitation does not increase overall with increasing size of anthracite, but rather that at the smaller level no increase was noted within the petrographic entities with the exception of durain (Figure 5).

Effect of Preheat Treatment on Decrepitation

Several prior investigations have noted that anthracite which has been subject to gradual heating showed a reduced tendency to decrepitate when subjected to extreme temperature gradients (Miroshnichenko, 1938; Skomorochov, 1938; Clendenin et al, 1945; Erenburg, 1954). Work at The Pennsylvania State University (Delvaux et al, 1957) indicates that a critical heating rate exists for each anthracite which if exceeded results in increased decrepitation. Also indicated is the existence of a critical temperature level. Once this is reached, the rate of heating does not effect decrepitation. Neither the critical heating rate nor the critical temperature has as yet been determined conclusively.

The previous work referred to was carried out with lump size anthracite while the present study was confined to smaller sized petrographic entities of anthracite. Previous experiments had preheated to relatively high temperatures at low heating rates: to 1400°C. at a rate of 1.3°C. per minute (Miroshnichenko, 1938; Skomorochov, 1938), and to 1400°C. at a rate of 5°C. to 6°C. per minute (Erenburg, 1954). In an attempt to reduce the required process time as well as the cost of pretreatment, higher rates of heating to lower ultimate temperatures were investigated.

For these experiments clarain particles of "Anthracite B" were chosen. The particles were subjected to preheat treatment at a uniform heating rate (14°C. per minute) the preheating being carried out to varying temperatures. The particles were then cooled and each subjected to thermal shock at 900°C. The results of these investigations, presented as Table 3 and Plate V, show that preheating the grains to 900°C. prior to shock heat definitely reduced the visible decrepitation to a marked extent. More data is necessary on preheating each of the petrographic entities to different maximum temperatures and particularly at reduced heating rates in order to determine the mode as well as the extent of preheat treatment which will maximize thermal stability. Previous work (Clendenin et al, 1945) has shown that while some coals which had a lower physical stability before thermal treatment showed an increase in strength after the treatment, other coals demonstrated reverse behavior. Other work (Delvaux et al, 1957) has even indicated that none of the supposed causes of decrepitation, volatile matter and moisture evolution, and pore structure, are really useful in determining the degree of decrepitation which anthracite undergoes when subjected to thermal shock, but rather that certain types of coals, aside from these characteristics, are more stable than others. The key to this problem might well be in identifying the decrepitation characteristics of the petrographic entities and determining the tendency of the particular anthracite to decrepitate from the decrepitation characteristics of the petrographic entities and the relative amounts of the various entities present in the coal.

Table 3

Effect of Preheat Treatment on Decrepitation

Maximum Temperature of Preheat Treatment (°C.)	Observations During Preheat Treatment and Upon Thermal Shock
500	No visible decrepitation during preheat. No immediate cracking on shock heat, but after 3-4 minutes of shock heat, visible decrepitation occurred.
600	No visible decrepitation during preheat. Some immediate, and great deal of delayed cracking occurred upon shock heat.

Table 3 (Cont.)

Maximum Temperature of Preheat Treatment (^{o}C.)	Observations During Preheat Treatment and Upon Thermal Shock
700	No visible decrepitation during preheat. On shock heat a great deal of immediate cracking and very little delayed cracking took place.
800	Few small cracks appeared on preheat. No immediate cracking and very little delayed cracking on shock heat.
900	No visible decrepitation occurred either on preheat treatment or on shock heating.

Clarain particles of +2" fraction of "Anthracite B" preheated at rate of 14^{o}C. per minute to varying temperatures, cooled, and subjected to shock heat at 900^{o}C. for 15 minutes.

On the basis of the experiments performed an attempt has been made to rank the petrographic entities in the order of increasing resistance to decrepitation. Work done on the effect of heating rate on decrepitation indicates that fusain and clarain decrepitate to a greater extent than vitrain and durain when subjected to gradual heating.

Visual observation of the particles when subjected to shock heat as well as the resulting product (Table 2) shows that fusain undergoes a greater degree of decrepitation than any of the other entities. Clarain also decrepitates to a greater extent than either vitrain or durain when subjected to shock heat; the cracking occurs at a lower temperature of shock heat and is much more violent than that exhibited by the other lithotypes.

Weight loss studies (Figures 4 and 5) show that fusain undergoes a much greater loss in weight than any of the other particles. Figures 4 and 5 might be interpreted as showing vitrain to be less resistant to decrepitation than clarain, but the results of observing the particles when subjected to gradual heating at varying rates as well as shock heat at different temperatures (Table 2) show that in the overall picture clarain is much less resistant to thermal decrepitation than vitrain.

The classification of the petrographic entities of "Anthracite B" in the order of increasing resistance to thermal decrepitation on the basis of the investigation would be, 1) fusain, 2) clarain, 3) vitrain, 4) durain. More data would be necessary to establish the variation among anthracites of the decrepitation which these entities undergo.

Conclusions

From the work carried out the following conclusions are drawn:

1. A decrease in weight loss accompanies increasing heating rates for the range of heating rates employed (Figure 1).

2. The critical temperature does not vary significantly for the three anthracites studied, being in the range of 625^{o}C. to 675^{o}C. (Figure 2).

3. Decrepitation is not an entirely immediate phenomenon, but tends to increase as the total heating time is increased (Figure 3).

4. Decrepitation, as measured by the weight loss, either decreases to a slight extent or shows no change with increasing particle size for the petrographic entities studied with the exception of durain which shows a slight increase (Figure 5).

5. Preheating the particles prior to shock heat reduced the visible drecrepitation to a marked extent.

6. The studies of the petrographic entities of anthracite indicate a resistance to thermal shock in the increasing order of 1) fusain, 2) clarain, 3) vitrain, 4) durain.

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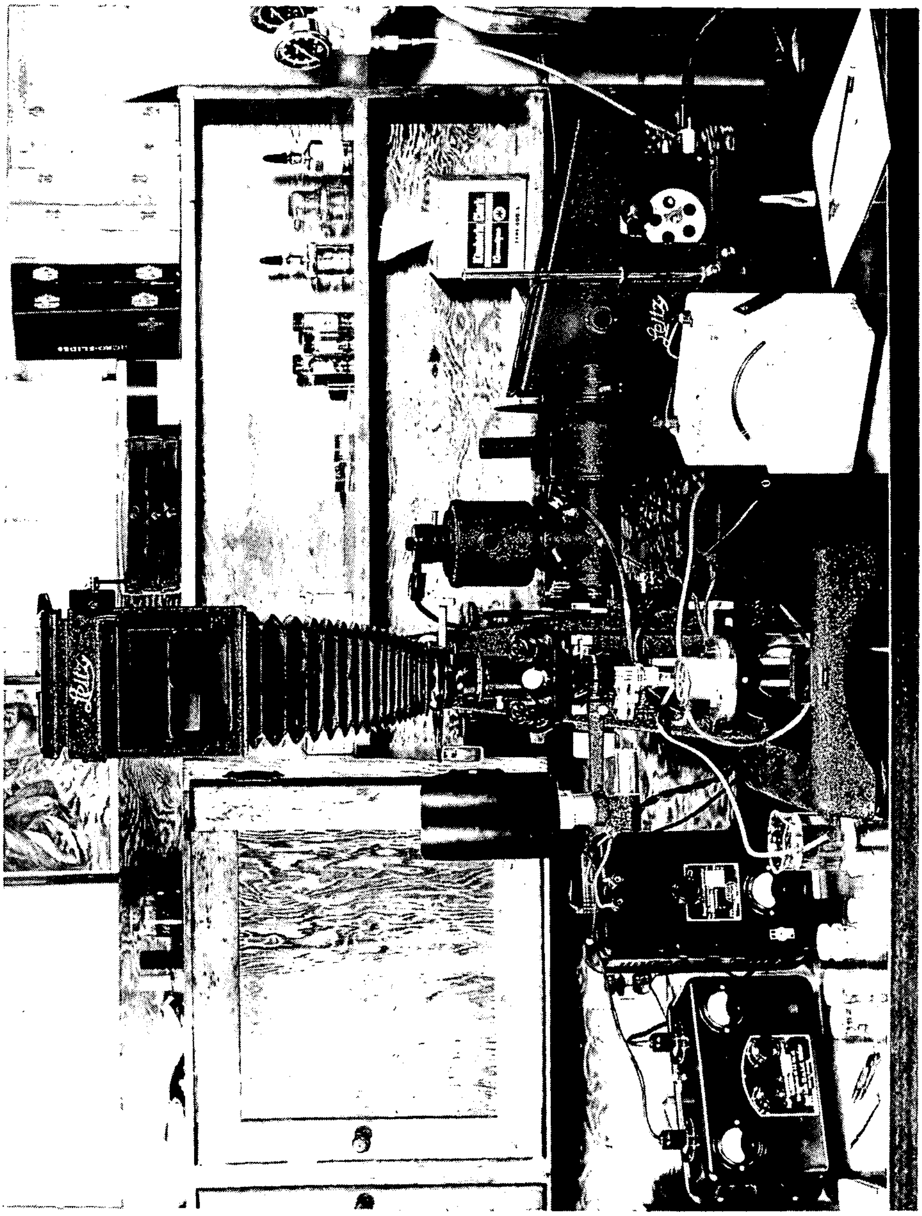


PLATE I

Leitz Panphot with Heating Stage

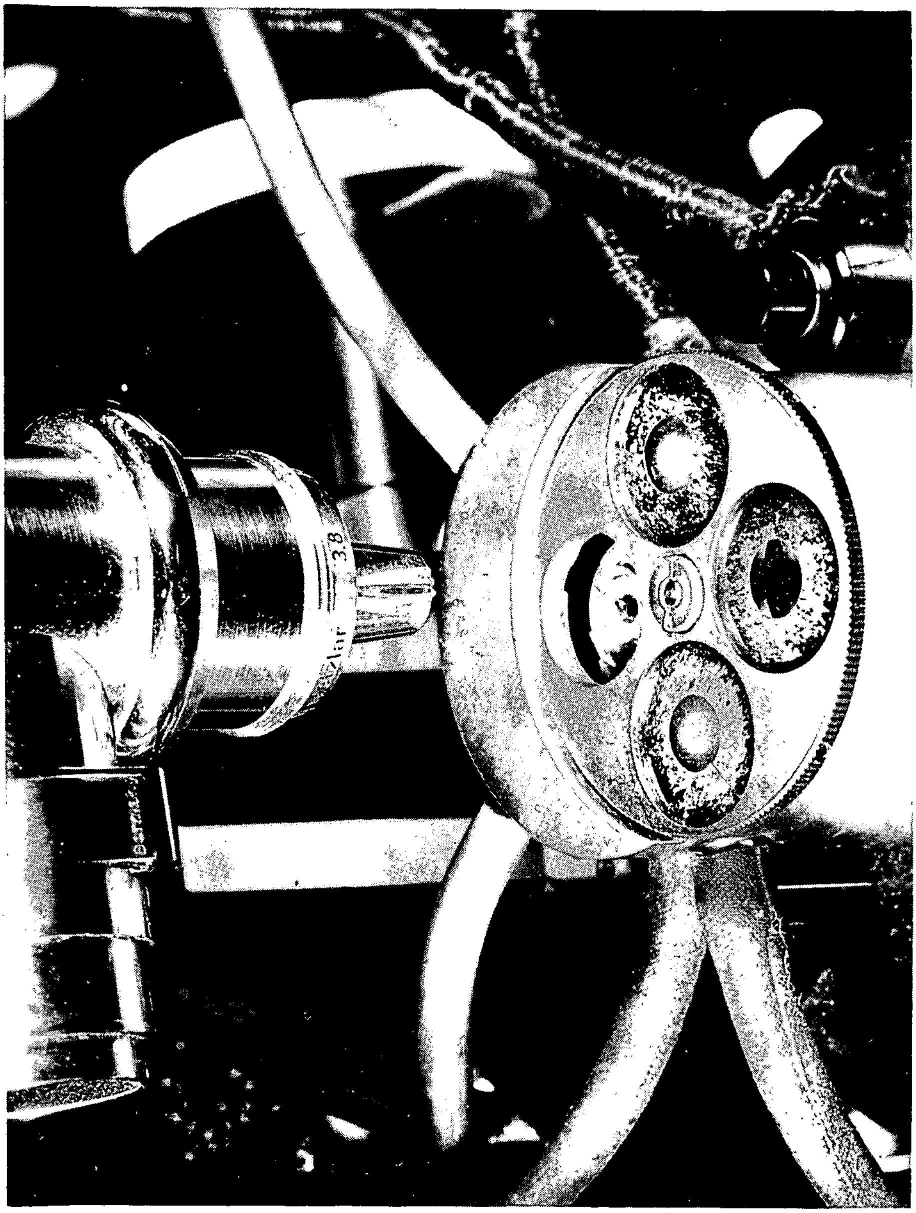


PLATE II

Close-Up of Heating Stage with a Grain of Anthracite in the Micro-Furnace

VITRAIN
Anthracite "B"

CLARAIN
Anthracite "B"

DURAIN
Anthracite "B"

FUSAIN
Anthracite "C"

PLATE III

Types of Petrographically Distinct Particles Investigated

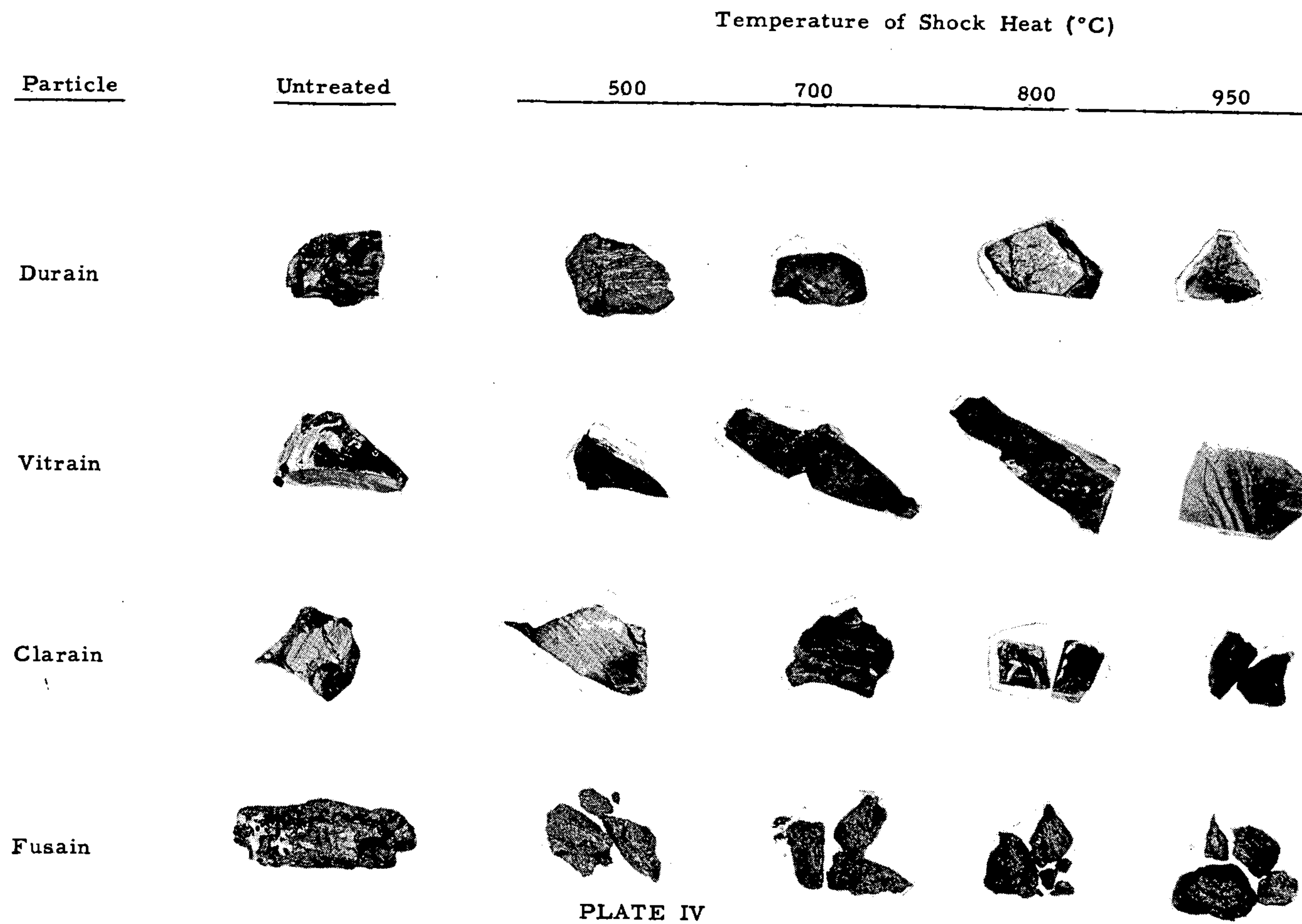
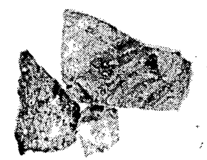


PLATE IV

Effect of Shock Heat on Petrographically Distinct Grains of Anthracite

Particles from "Anthracite B" shock heated from
10 to 15 minutes in a nitrogen atmosphere.



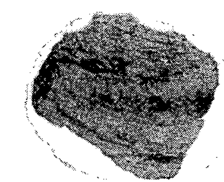
No Preheat Treatment

Preheated to 500°C

Preheated to 600°C

Preheated to 700°C

Preheated to 800°C

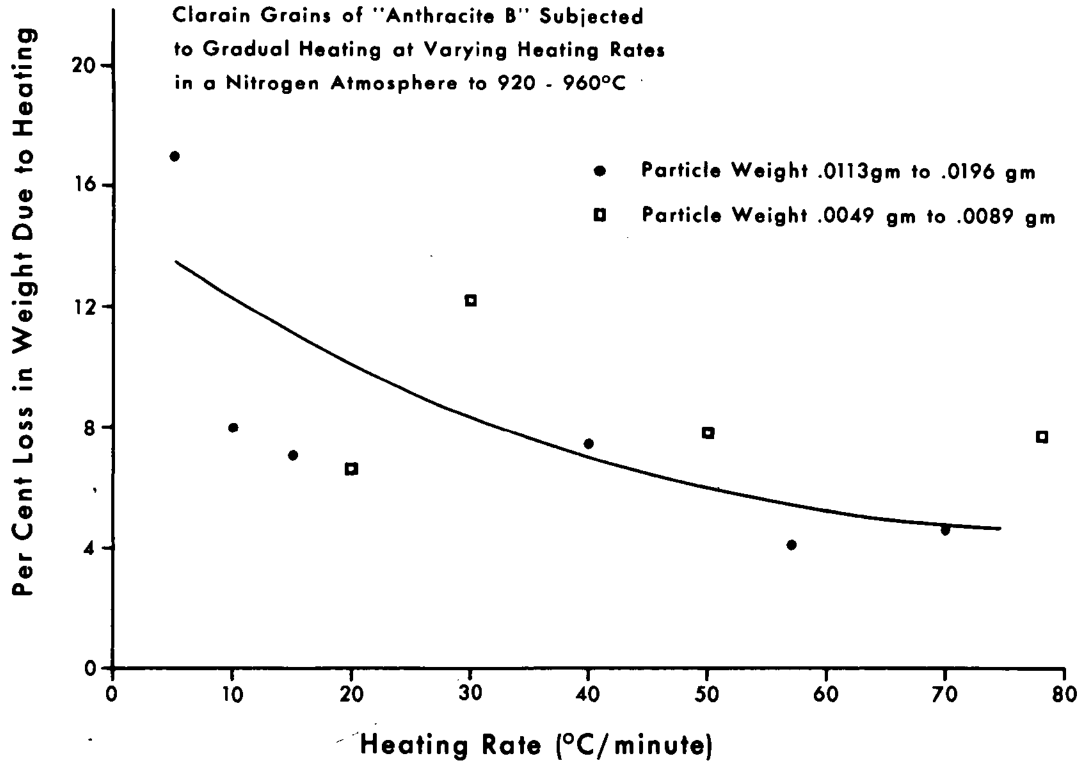


Preheated to 900°C

PLATE V

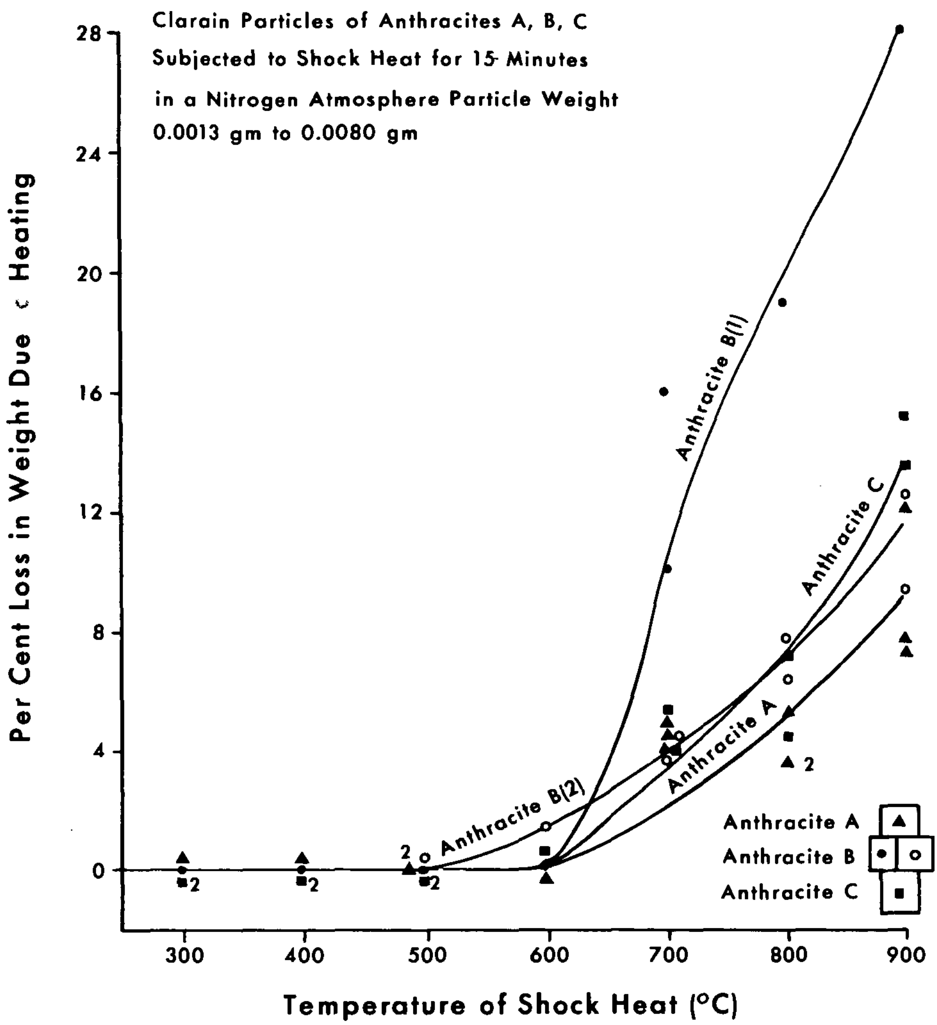
Effect of Preheat Treatment on Thermal Stability of Anthracite Particles

Clarain particles of "Anthracite B" preheated to different temperatures at a heating rate of 14°C per minute, cooled, then shock heated for 15 minutes at 900°C in a nitrogen atmosphere.



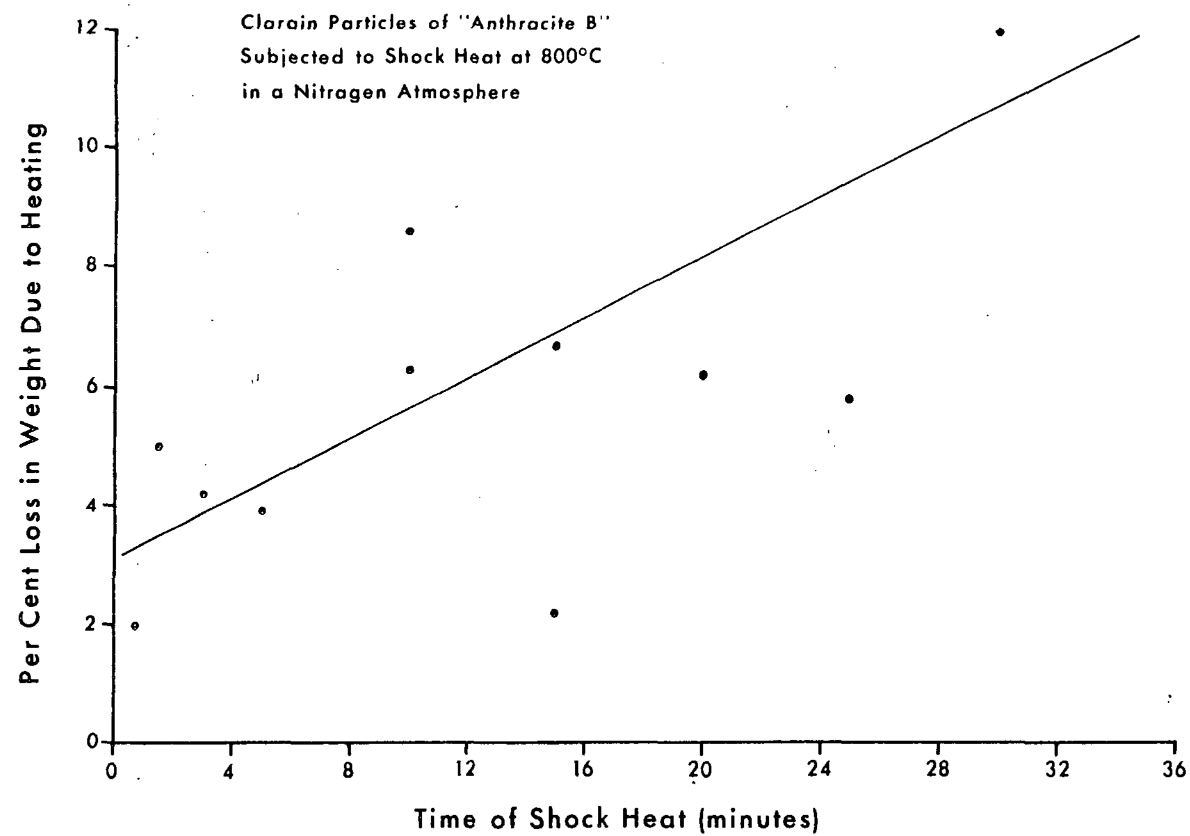
RELATION BETWEEN LOSS IN WEIGHT
AND
HEATING RATE

Figure 1



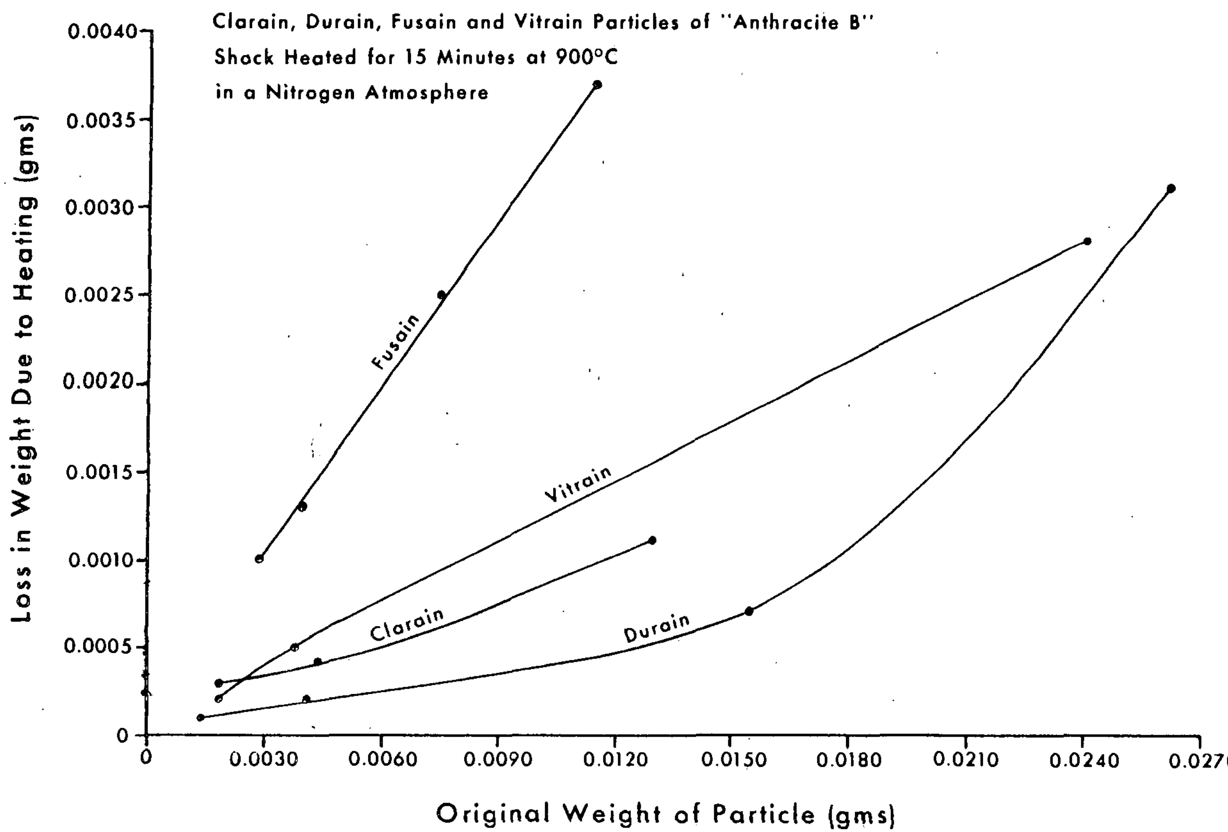
RELATION BETWEEN LOSS IN WEIGHT
AND
SHOCK HEAT TEMPERATURE

Figure 2



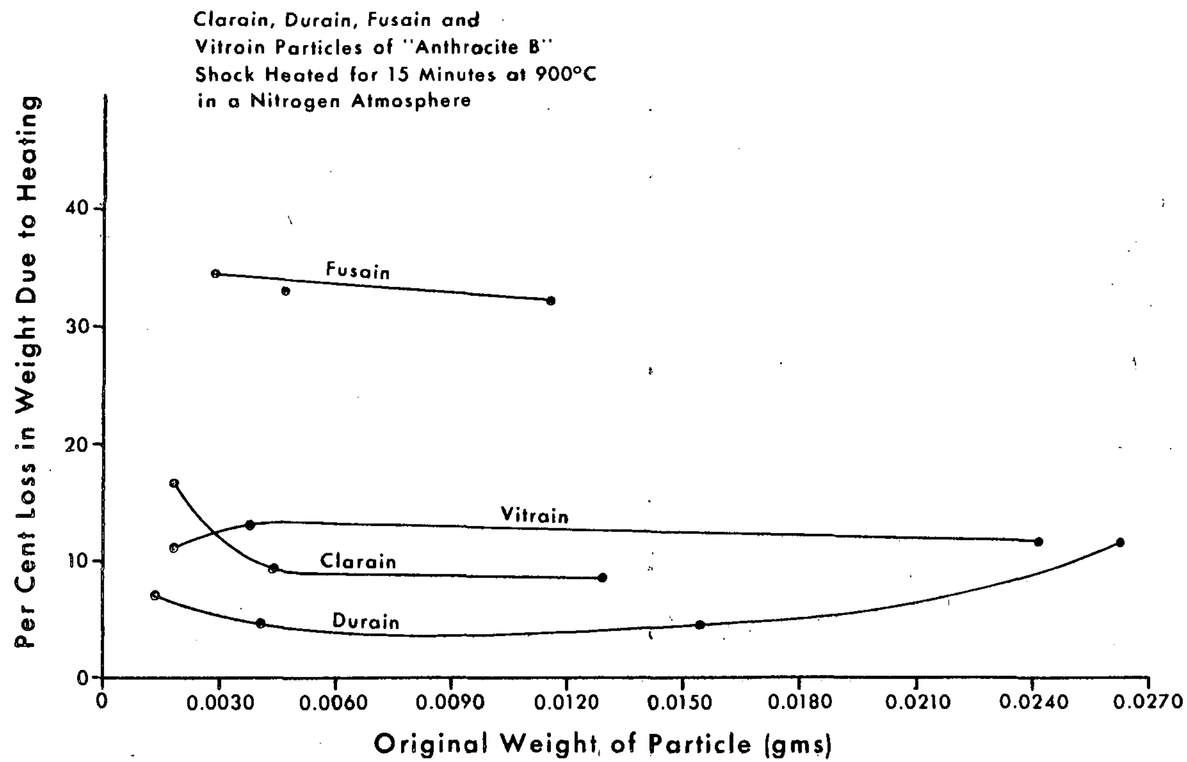
RELATION BETWEEN LOSS IN WEIGHT
AND
TIME OF SHOCK HEAT

Figure 3



RELATION BETWEEN LOSS IN WEIGHT
AND
TIME OF SHOCK HEAT

Figure 4



RELATION BETWEEN LOSS IN WEIGHT
AND
ORIGINAL PARTICLE WEIGHT

Figure 5