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THE EFFECTS OF PREOXIDATION ON THE SWELLING AND
SOFTENING OF BITUMINOUS COALS

Technical Report 20

By
D. J. Maloney
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MASTER

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The Pennsylvania State University
Coal Research Section
University Park, Pennsylvania

U. S. DEPARTMENT OF ENERGY

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COAL RESEARCH SECTION
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ABSTRACT

A study was conducted to evaluate the applicability of a DuPont 942-TMA (Thermomechanical Analyzer) dilatometer system for the characterization of the swelling and softening properties of caking coals. The results of this investigation demonstrate the utility of this dilatometer system. Several parameters are clearly defined with this unit which are characteristic of the plastic transitions occurring upon carbonization. These include softening, dilation and resolidification temperatures and volume contraction, expansion and total dilation values.

The transition parameters measured with the 942-TMA unit are found to be influenced significantly by coal particle size, dilatometer load, and heating rate. All transition temperatures exhibit marked increases with increasing heating rate. Softening temperatures decrease with increasing load and particle size. Dilation temperatures are essentially independent of dilatometer load effects and resolidification temperatures are independent of load and particle size over the range of conditions used in this study. Volume contraction and expansion values show an increase with decreasing coal particle size. Volume expansion values also exhibit strong heating rate and load dependencies.

A series of caking coals was examined with this dilatometer unit under the following operating conditions: 50°C/min heating rate, 1g dilatometer load and -200 mesh coal. Wide variations in plastic behavior are observed as a function of coal rank. The onset of softening, initial dilation and resolidification temperatures all

pass through minima in the range of caking coals. Dilation values pass through a maximum for coals of vitrinite reflectance in the range from 0.90 to 1.55 (Mean-Max. R_0) or carbon content in the range 83.5% to 87% carbon (daf). Coals with abnormal amounts of exinites, inertinites, ash or oxygen behave differently from most coals of equal rank.

Two high swelling coals were oxidized to various levels of weight gain (as monitored with a Cahn electrobalance) and analyzed with the 942-TMA dilatometer under the following conditions: 50°C/min heating rate, 1g dilatometer load, and 200 x 230 mesh coal. It is found that as the temperature of oxidation rises, for a given level of weight gain, the reduction in plastic behavior of a coal becomes greater. Additions of relatively small amounts of oxygen (1-2% by wt.) to a coal are found to bring about dramatic changes in swelling and softening properties. In general, oxidation brings about substantial reductions in volume expansion and contraction, increases in softening and dilation temperatures, and a slight reduction in resolidification temperatures. For coals which exhibit rather high Gieseler fluidities, slight oxidation is found to bring about an increase in expansion prior to destruction of swelling properties.

The results of this work point up the great difficulty involved in obtaining truly fresh "unoxidized" coal samples. Storage of fine coal particles for extended periods of time in atmospheres with even slight oxygen concentrations show signs of weathering.

Weathering studies indicate that exposure of an HVA coal (PSOC-1099) to dry air at ambient temperature has much less effect on subsequent swelling and softening properties than does exposure

to moist air. This suggests that water interacts with oxygen groups on the coal surface to accelerate the weathering process. Finally, it is shown that plastic properties of an oxidized coal may be partially restored simply by grinding to expose new surface.

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1. INTRODUCTION

In light of current shortages of domestic natural gas and petroleum the American people are being forced to seek alternative fuel sources. One of the most obvious and readily available fuel alternatives is the increased utilization of the enormous coal reserves in the United States. Coal is found in over 30 of the 50 states and accounts for more than 90 percent of the proven fossil fuel reserves in the United States (1). Much of this coal is suitable for direct use in combustion units (clean burning, low sulfur content). In addition, coal gasification and liquefaction technologies provide methods for the production of clean burning fuels from relatively dirty, high sulfur, coal precursors.

The greatest energy consumers in this country are located in the highly industrialized urban centers of the midwest and the east. The large majority of coals found in these areas are of the caking variety. Caking coals present some unique problems in various gasification and combustion schemes.

When caking coals are heated in the absence of air, they soften (i.e. become plastic), agglomerate, and as gases and vapors are evolved, swell to form a coke. These properties make some coals impractical for direct use in gasifiers and some combustion units because agglomerates impede gas flow, leading to poor mixing in reactors and eventual plugging.

The most common method of removing this caking behavior is preoxidation of the raw coal at temperatures below the softening point of the coal. This method is very effective in removing

softening properties. However, preoxidation leads to a reduction in the calorific value of the coal; and it involves an extra processing step which is costly and which reduces overall thermal efficiency. Also, very little is known about the effects of preoxidation on the behavior of coals during gasification.

With the need for increased domestic coal utilization and considering the problems encountered with caking coals, it is desirable to examine closely the caking properties of bituminous coals and the subsequent effects of preoxidation upon these properties. The following study is an attempt to quantify the swelling and softening properties of selected coals and to monitor the changes in these properties upon mild oxidation.

2. SURVEY OF THE LITERATURE

It is well known that coals of certain rank (high volatile C bituminous to low volatile bituminous) soften and become plastic upon heating (350-500°C). These plastic coal particles agglomerate and, as gases and vapors are evolved, swell to form cokes. This phenomenon is essential for the production of coke and, as such, has been of great interest to the coal chemist for many years. The importance of high quality metallurgical coke in the production of steel has brought about the development of hundreds of test methods aimed at predicting the behavior of coal in the coke oven (2,3). The many results of these various test methods, coupled with differences in the interpretations of these results, have led to the rise of several theories on the causes of plasticity in coal.

In addition, workers in the field have been concerned with the problem of low temperature oxidation of coals. Mild oxidation of a good coking coal has been shown to cause sharp reductions in coking power. Storage of a coal for a few months in ambient air leads to the production of an inferior coke, and in some cases the coal becomes useless (as a source of coke) and must be disposed of (4).

The oxidation problem is not restricted to coking coals alone. Low temperature oxidation is responsible for the spontaneous combustion of coal piles or exposed coal seams. Accordingly, many investigators have looked at the low temperature oxidation of coal.

In the next chapter, various test methods for the analysis of caking properties will be reviewed along with several of the more widely held theories of the mechanisms of coke formation. In addition,

the results of several oxidation studies will be presented. This material will be looked at in an effort to provide some insight into the causes of losses in plastic properties upon low level oxidation.

2.1 Test Methods

Many test methods have been used in evaluating the ability of bituminous coals to produce commercial coke. Most of these techniques have been reviewed by Brewer (3) in 1941 and later by Loison and co-workers (2) in 1963. The principles involved in the various test methods range from macroscopic and microscopic examinations of the coke and the parent coal to small scale coke oven simulation. Most of these tests are empirical in nature and require that strict specifications be followed. Brewer has divided the many test methods into several classifications. For convenience, this classification system will be followed in discussing some of the various techniques that are presented in the literature.

2.1.1 Direct Observation Test Methods

Direct observation of coal in combustion units was probably the first method used to study the coking phenomenon. Through observations with the naked eye one can obtain a rough and qualitative indication of plastic behavior.

Microscopic examination provides more detailed information. Softening and resolidification temperatures can be fairly well defined, and one can derive information about the behavior of individual macerals. This type study is limited, however, in that the information obtained is of a qualitative nature only; and this technique provides little indication of swelling phenomena. The work of Mott (5) is a good illustration of the uses of these methods.

More recently workers have applied polarized-light optical microscopy techniques to the study of coals and cokes with great success (6,7). Polarized-light techniques are used to study the development of anisotropic mesophase structures during the carbonization process. The anisotropic structures are of great importance in that they have a strong influence on the strength and reactivity of the coke. These techniques are being used in efforts to establish a more fundamental picture of the mechanisms of conversion of coal into coke.

2.1.2 Agglutinating and Free-Swelling Test Methods

Test methods in this classification are designed to define some "swelling-index" or "agglutinating value" which will give an indication of a coals behavior in the coke oven.

In free-swelling or agglomeration tests, a sample of finely ground coal ($< 250 \mu\text{m}$) is placed in a crucible or tube and is heated according to a fixed heating rate, until a temperature of about 800°C to 900°C is attained. The "agglomerating-index" or "swelling-index" is based upon the nature of the residue from the heat treated coal. These tests indicate the tendency of coal particles to fuse together and form a compact mass and they allow a clear limit to be drawn between caking and non-caking coals. The degree of swelling can be assessed from the ratio between the volume of the coke obtained and the initial volume of the coal or by comparing the profile of the coke obtained with a series of reference profiles. The ASTM standard for Free-Swelling Index measurement (8) is a prime example of an agglomeration test.

Agglutination tests involve mixing coal with an inert substance and then carbonizing the mixture at a specified heating rate. The mechanical strength of the resulting "coke" button is then determined by crushing or abrasion tests. Agglutination values thus obtained reflect the ability of the plastic "coal" to bind together an inert filler. These values are directly related to coke strength and are used to assess the potential of a coal for commercial coke manufacture.

Agglutination test methods have been summarized and reviewed critically by Marshall and Bird (9). Brewer (3) later added to this work. No major new developments have been reported since the work of Brewer in 1941.

Both agglutination and free-swelling test methods are empirical in nature and as such are highly dependent on heating rate, sample size and apparatus geometry. These methods do provide some indication of the coking potential of a coal; however, they do not always provide a close correlation with the strength of commercial coke obtained. For this reason several large scale box and muffle tests were developed in the early 1900's. These tests simulate actual coke oven conditions and give a better correlation with the coking potential of a coal.

2.1.3 Gas Flow or Foxwell Test Methods

The gas-flow or Foxwell test methods depend upon the change in resistance to flow of a stream of inert gas caused by back pressure developed in a plug or column of heated coal (3). For coking coals this resistance or pressure begins to increase when the coal begins to soften, rises to a maximum, and then usually decreases to its

original value. The data usually recorded are the maximum pressure and the temperatures of initial softening and of maximum pressure. The sample is usually sized and is often mixed with an inert material so that, in most cases, the sample is not representative of the coal. In addition, there is some dispute as to the exact physical meaning of the maximum pressure value measured in this test.

2.1.4 Plastometer Test Methods

Plastometer test methods are designed to measure the resistance of a heated coal charge to shear caused by an applied known torque. Two general adaptations of this principle have been made. A variable-torque plastometer was first designed by Davis in 1931. In this type of apparatus, coal is placed in a horizontal cylindrical retort which is rotated at a uniform speed. A spring loaded shaft with rabble arms is located inside the retort. The coal and retort are set in motion and the torque acting on the shaft is assessed by measuring the deformation of the spring.

The constant torque plastometer was later developed by Gieseler. The general set up for this apparatus is similar to the above. The difference arises in that the retort remains stationary and the rabble armed stirrer is rotated at a constant torque. In this method, the change in the rotation of the stirrer is recorded versus temperature.

Plastometer systems are useful in that they provide several parameters for the analysis of plastic properties. The data most often reported are the softening and resolidification temperatures, the maximum fluidity (corresponding to minimum torque or maximum rotation), and the temperature of maximum fluidity.

Softening and resolidification temperatures determined in the plastometer are not absolute values. These temperatures are determined by convention. That is, they are taken as the temperatures at which a certain minimum value of fluidity is reached. Fluidity data such as maximum rotation or minimum torque are related to the viscosity of the plastic material. However, these are not absolute viscosity measures; and one must be careful when assessing the data obtained from these methods.

2.1.5 Extrusion Test Methods

Extrusion type test methods employ an apparatus having an orifice through which softened heated coal is forced under an applied pressure. The data obtained provides a measure of the fluidity which the coal undergoes and has been applied qualitatively in interpreting some of the fluid phenomena observed with coal (3). The conditions under which these type test methods are carried out do not compare well with actual coking of a coal charge in commercial coke ovens. Consequently, these test methods have not been widely used in the analysis of caking coals.

2.1.6 Penetrometer and Dilatometer Test Methods

Penetrometer test methods are used in efforts to assess the degree of softening a coal mass has undergone during heat treatment. Pelletized coal samples are loaded into the apparatus and the penetrometer probe is centered atop the pellet. In most cases, this probe consists of a needle or thin wire loop. Upon heating, the probe penetrates the softened coal charge and the degree of softening is judged from the depth of penetration of the probe. Since penetration is arrested upon resolidification of the sample, these techniques are

especially good for determining resolidification temperatures. They also provide information on softening temperatures. The values measured with penetrometer systems are not absolute; changes in pelletizing pressure and probe dimensions lead to significant changes in these values. One must keep this in mind when analyzing data from penetrometer systems.

Dilatometer test methods are used to measure the expansion and contraction of a coal sample under controlled heating conditions. The samples used in these techniques are most often cylindrical pellets or "pencils" obtained by compression of pulverized coal. These samples are loaded into the apparatus and the dilatometer probe or "piston" is brought to rest on top of the pellet. During the test, expansion (or contraction) of the heated coal charge is indicated by the vertical displacement of the probe.

Many types of dilatometers have been developed. Most of these apparatus are used to study softening and swelling of coal during semi-coke formation (350-500°C). The more common instruments in use today are the Audibert-Arnu dilatometer and the Ruhr dilatometer. These methods provide several characteristic parameters for study. In addition to contraction and expansion values, they are used to gather information on softening and resolidification temperatures and the temperatures of initial dilation and maximum expansion.

In a typical dilatometer system, the coal pellet must support the weight of the dilatometer probe. Often, an added load is placed upon the probe so that the sample must resist a substantial force. The magnitude of this force has a definite effect on the values of the

parameters measured. This should be considered when analyzing data from dilatometer systems.

Both penetrometer and dilatometer test methods are empirical in nature. The major difference between the two arises from effects caused by changes in the relative cross-sectional areas of the probe surfaces that bear on the coal sample. In fact, under high enough loads or with very fluid coals the dilatometer probe may behave as a penetrometer. Due to the empirical nature of these tests the actual magnitude of pressure or stress developed in the heated coal mass during its carbonization is not determined.

2.1.7 Chemical Test Methods

Chemical test methods have been used to assess the coking potential of coals also. When solvents, such as pyridine, are absorbed by a coal, there is a resultant swelling. The degree of swelling is related to the rank of the coal and the suitability of a coal for coking can be predicted to a limited extent from its swelling property in the solvent.

In addition, solvent extraction work has been shown to be of some use for evaluating the coking potential of certain coals (10). Some workers believe that the quantity of a certain extract (chloroform) is directly related to the coking behavior of coal. These methods are not used routinely in commercial practice but have been used in more fundamental work. There is some debate in progress as to whether the solvents used extract material already present in the coal or whether these solvents chemically attack the coal to produce the extractable material.

2.2 Factors Affecting Plastic Properties

Most of the studies conducted on caking coals have been directed at determining the behavior of coals in the coke oven. These tests employ standard conditions, and the results are analyzed from the standpoint of the quality of the coke produced. This is sufficient from an industrial viewpoint; however, if one wishes to gain a fundamental understanding of the coking mechanism, more detailed studies must be performed. In fact, several authors have published results of such work. These studies examine the variables; coal rank, petrographic composition and carbonization conditions, and their effects on the coking process. Some of the results of this work are presented in the following section.

2.2.1 Nature of the Coal

Of primary importance in understanding the swelling and softening phenomena observed on heat treatment of some coals is a knowledge of the nature of the starting material. For this reason, many attempts have been made to correlate plastic properties with various coal rank parameters (2,3). In addition, carbonization studies have been made on individual petrographic constituents in efforts to examine the contributions of the individual macerals to overall plastic behavior.

The plastic properties of coals vary considerably with rank. In fact, it is the ability of a coal to agglomerate and form a cake upon carbonization that is used by the ASTM (11) as a requisite physical property to differentiate semi-anthracite from low-volatile bituminous coal and, also, high-volatile C bituminous from sub-bituminous A coal. Within this range of coals, plastic properties

reach a maximum for coals with 25 to 30% volatile matter. The swelling as measured by dilatometry, exhibits a maximum for a volatile matter (VM) of about 25-28%, while the Gieseler fluidity reaches a maximum at about 28 to 32% VM content (2).

Carbonization studies of individual macerals have shown that for a given degree of coalification, the component macerals behave rather differently. Vitrinites obtained from coals in the caking range exhibit a fair degree of fluidity upon heat treatment. In general, vitrinite is the most abundant maceral found in coal and, as such, is the principal material responsible for plastic behavior.

Exinites differ from vitrinites of the same rank by a higher hydrogen content and a higher VM content. These macerals exhibit a very high fluidity and an expanded plastic range. Coals which contain abnormally high amounts of exinite exhibit different behavior due to their high fluidity.

Inertinites, on the other hand, behave as the name implies. Macerals such as fusinite and micrinite behave like inert substances during carbonization. These substances are characterized by high carbon content and low hydrogen and VM contents. Coals high in inertinites exhibit little agglomeration or swelling.

The plastic properties of a coal are the result of the properties of the macerals of which it is composed. These properties depend on the manner of distribution of the macerals and, in particular, on the greater or lesser dispersion of the exinite and inertinite within the vitrinite. The degree of dispersion determines the amount of interaction of the different macerals during their fusion (2).

2.2.2 Heating Rate

Whatever the method of observation employed, an increase in the heating rate enhances the plastic properties of a coal; the fluidity and swelling are increased; and the plastic range is broadened (2). Coals which show no caking potential under commercial coking conditions, soften and may swell when heated rapidly. Conversely, it has been shown that all coals, irrespective of their rank, can be carbonized without showing any swelling provided the heating rate is sufficiently slow (12).

2.2.3 Particle Size

Due to sample size limitations, most laboratory devices do not lend themselves to the study of a wide range of particle sizes. Some work has been done looking at fine particle sizes ($< \text{hundredths of } \mu\text{m}$). These studies indicate that very fine grinding reduces plastic properties. However, it is not clear whether these results are due to the increased ease of oxidation of more finely ground coal or to maceral and mineral segregation on grinding. Studies conducted in a Hoffmann dilatometer, which accommodates itself to rather coarse coal samples, have shown that the effect of particle size varies according to the type of coal and to the petrographic constituents (2).

2.2.4 Pressure

Another variable which has a marked effect on coking properties is the pressure of the carbonizing atmosphere. Under vacuum conditions for example, coals which normally soften swell and cake no longer give a coherent residue. In contrast to this, when coal is carbonized under high pressure, the caking of the particles is enhanced and swelling increases (13).

2.2.5 Applied Pressure or Load

In dilatometer and penetrometer studies, where a known weight or load is applied to the probe, plastic properties vary with the applied load. Pressure effects vary somewhat with different coals but in general, an increase in applied load brings about a decrease in the softening temperature and a decrease in dilation (2).

2.3 Mechanisms of Coke Formation

The great number of test methods employed in the study of the plastic properties of caking coals, coupled with differences in the interpretations of the data generated in these tests, has led to the development of several theories on the mechanism of coke formation. In most cases, these theories actually involve a series of mechanisms to explain the softening, swelling, and resolidification phenomena observed in the coking process. Several good reviews of the pertinent literature are available (2,3,14). In the following section, some of the more widely held theories of the mechanisms of coke formation are presented.

2.3.1 Mechanisms of Softening

The mechanisms proposed to explain softening may be classified as either physical or physiochemical. In the physical theories, softening is considered as a result of "melting" due to an increase in thermal agitation and is similar to that which thermoplastic materials undergo (2). The various physical theories differ with regard to the hypothesis put forward on the nature and the mode of action of the fusible (melt) fraction. In the physiochemical theories, softening is considered a consequence of pyrolysis, being due either

to the pressure of the gas produced or to the formation of a fluid substance which plasticizes the mass of coal.

2.3.1.1 Theory of Homogeneous Melting

According to a theory put forth by Audibert (15) and Audibert and Delmas (16), coal is a mixture of organic compounds which, upon heating, undergoes a paste-like melting to form a fused mass. Concurrent with this, the fused coal material undergoes thermal decomposition which results in the formation of solid infusible products and gases or vapors. Complete fusion of the coal will occur at a definite temperature if the melting point is below the decomposition point. However, thermal decomposition of coal almost always begins below the softening point; and, in these cases, fusion is incomplete. Audibert notes that the degree of fusion is strongly dependent on the heating rate. Complete fusion of the coal is observed if the heating is sufficiently rapid or does not take place at all if the heating is too slow. This theory is consistent with these observations. As the heating rate increases, the softening point is not modified significantly because melting is a physical mechanism; however, one expects the pyrolytic (chemical) reactions responsible for producing the infusible material, to shift to higher temperatures.

2.3.1.2 Partial Melt Theory

Audibert's interpretation of the coking process agrees quite well with the experimental results of many carbonization studies. However, this theory fails to account for the strong dependence of coking properties on changes in the pressure of the carbonizing atmosphere. For example, coals which form good cokes exhibit a marked

reduction of fusibility when carbonized under vacuum conditions.

This pressure dependence may be explained if one considers that only a fraction of the coal melts or fuses and that the fluidity of this fraction is sufficient to give the whole coal a certain plasticity.

Several investigators (10,17-20) have proposed theories on the partial melting of coal. According to these theories, plastic properties are the result of some "coking-principle" which is present in the coal. It is thought that this "coking-principle" is an extractable hydrocarbon fraction called "bitumen". A common view is that the pyridine or benzene soluble fraction is responsible for agglomeration and swelling properties.

Illingworth (10) refined these theories by splitting the pyridine soluble "bitumens" into β -compounds (pyridine soluble, chloroform insoluble) and γ -compounds (pyridine and chloroform soluble). From his studies of the thermal stability of these bitumen fractions and of the coal residue, he concludes that the plasticity of coal is due to the γ -compounds becoming liquid. The theory follows that the gamma compounds fuse the various residues from the coal substance into a coherent mass. However, these liquid γ -compounds are thermally unstable and begin to decompose. Upon progressive destruction of the γ -compounds, coal passes from a state of maximum "fluidity"* through increasing degrees of "viscosity", until a very viscous or semi-solid state is approached, and ultimately to a condition where there is an absence

* Illingworth cautions that the terms "plasticity", "fluidity" and "viscosity" should be taken more as suggesting analogous conditions than as dogmatic statements regarding the actual physical states.

of any plasticity. The author states that there is a critical γ -compound concentration, below which coking does not occur (5.5%).

Shimmura (19) and Cockram and Wheeler (20) subdivide the γ -compounds into γ_1 (soluble in light petroleum), γ_2 (insoluble in light petroleum, soluble in ethyl ether) and γ_3 (insoluble in light petroleum and ethyl ether) fractions. The γ_1 -fraction consists mainly of saturated and unsaturated hydrocarbons and is thought to be responsible for the agglutination or fusion action of coal. The γ_2 -fraction is composed of compounds which are called "resin-acids", "resin-esters" and "resinols", while the γ_3 -compounds are comprised of "resenes". Shimmura concludes that the swelling observed during coking is due to the presence of the γ_2 - and γ_3 -compounds. In addition, the coking properties of coals are found to be not only a function of the bitumen constituents but are also influenced by the oxygen content of the pyridine insoluble coal residue (α -compounds).

2.3.1.3 Physiochemical Theories

In both of the physical melt theories presented above, the authors recognize that thermal decomposition of the fusible coal material begins to take place before the coal mass attains a truly fluid state. This close relationship between pyrolytic reactions and the development of plastic properties has led to the majority of authors (21-24) to consider softening as a consequence of pyrolysis. The theory, as stated by Oele (21), postulates that the plastic behavior of coal is due only to the formation of a liquid primary product of pyrolysis. It is believed that this liquid pyrolysis product plasticizes the remaining coal material.

Evidence for the "thermobitumen" or "metaplast" theory, as it is known, can be found in the solvent extraction work of Illingworth* (10) and of Dryden and Pankhurst (25). These authors show that a large increase in the amount of solvent extractable material is obtained after heating a caking coal to a temperature near the softening point (350-400°C).

Further evidence is supplied by vanKrevelen, Huntjens and Dormans (22) who have combined thermogravimetric, dilatometric and plastometric techniques to study the coking process. From the combined results of these studies, they conclude that the plastic transitions monitored by these techniques are not related to the physical properties of the coal substance but are the result of kinetic phenomena. Chermin and vanKrevelen (26) and Fitzgerald (27) have independently developed kinetic schemes to explain this behavior. These schemes are based upon a consecutive reaction theory. As postulated, the raw coal undergoes a kind of "depolymerization" to form a metastable intermediate. This "metaplast" then undergoes some cracking type reactions to form a semi-coke. Both of these reaction schemes assume first order kinetics for the formation of metaplast and the subsequent conversion to semi-coke. When compared with experimental results, they provide a satisfactory explanation of the coking phenomena.

Each of the theories discussed above interpret a number of facets of the complicated process of plastic softening of coal. The partial melting and complete melting theories in their original simple forms no longer find support; the respective views have drawn closer

* Illingworth does not attribute this increase to pyrolysis but believes that heat treatment is necessary to fully remove the γ -compounds present in the coal.

together. The various investigators seem to agree that softening is caused by plasticizing of the coal "macromolecule" and that the substance acting as plasticizer is formed either from the coal fractions of low molecular weight or (and perhaps mainly, but not exclusively) from primary decomposition products of lower molecular weight (22).

2.3.2 The Nature of the Plastic State

As yet, little mention has been made of the nature of the coal macromolecule or the plasticizing medium. A true understanding of the coking process is not possible without such information. In the following section, the nature of the plastic state will be examined more closely.

Mott (5,28,29) and Mott and Shimmura (30) emphasize the importance of the α - and β -compounds in the caking process. They point out that for fusion of the coal particles to take place the liquid hydrocarbon oil (γ_1 -compounds) must first wet the surface of the coal particles. For wetting to occur, two factors must be considered, namely, the nature (and amount) of the wetting agent and the nature of the surface to be wetted. Mott (28) argues that, on wetting, the interfacial phase is the seat of an electric field of great intensity and that the physical properties depend just as much upon the nature of the solid as upon the nature of the liquid. The best wetting agent for a good caking coal is a liquid paraffin hydrocarbon (similar to γ_1 -fraction). It follows that wetting by such a liquid is most effective when the surface to be wetted is rich in carbon and hydrogen or poor in oxygen (as in the case of good coking coals). Allinson and Mott (31) show that strongly swelling coals do, in fact, absorb

some of the tars produced during coking. Mott (29) notes that the yield of agglutinates increases on preheating of coal. He concludes that these wetting agents are not only produced by melting of chemical compounds but also by the thermal decomposition of larger molecules.

Foxwell (32) believes that the wetting action of the agglutinates is not caused by the affinity of the wetting agent for the wetting surface. Rather, he thinks that the fluid material is extruded, by internal gas pressure, from the interior of the particles. This internal pressure then causes the binding material to spread over the surface of contiguous particles.

From X-ray studies of the α -, β -, and γ -fractions of coal, Riley and co-workers (33) propose a crystallite structure for coal. Their results indicate that a bituminous coal consists of a structure of flat, aromatic lamellae, built up almost exclusively of carbon atoms and forming "turbostratic"* crystallites together with lamellae of "bitumen". These lamellae are essentially less aromatic than the "carbon" lamellae but sufficiently flat to form a turbostratic system. In a turbostratic system, the manner in which the more or less flat lamellae pack together when subjected to vibration (heating) depends upon the ease with which the lamellae can move with respect to each other. The mobility of the turbostratic system confers upon it its thermoplastic properties. The authors believe that bitumen lamellae are responsible for the high mobility experienced in bituminous coals.

*Turbostratic is a term which describes the crystallographic character of amorphous carbon crystallites. These consist of carbon atoms arranged in honeycomb-like flat layers, stacked parallel to each other but otherwise quite randomly oriented.

Through the use of a Spierer lens, Thiessen (34) identifies a micelle structure and demonstrates the colloidal nature of coal. Other workers (35-37) believe that the colloidal structure of bituminous coal is the cause of flowing, swelling and caking. Atkinson, Brewer and Davis (35) consider coal as a "coagel" in which micelles and other particles are dispersed. A necessary condition for the causation of plasticity in such a system is the formation of liquids which wet and soften the solid material and finally disperse the micelle and other material into solution. The authors cite evidence that these liquids are produced both by melting of certain definite chemical compounds and by the thermal cracking of larger molecules. They believe that while coal is being heated to the beginning of the plastic range, the organophilic nature of the micelles present causes much of this liquid formed to remain adsorbed on the solid surfaces and distributed throughout the intermicellar space. The solid particles are progressively softened by this liquid until finally the whole mass coalesces and forms a colloidal solution called the plastic state.

Lahiri (37) also believes the colloidal nature of coal is responsible for plasticity; however, he places a restriction on the nature of the colloidal constituents of coal. He considers coal as an "isogel" of which all molecules have analogous compositions and differ only in size. Coal is then composed of an assemblage of large molecules (or micelles) and smaller molecules. At temperatures below the gel point (T_g), such a system behaves as a mixture of insoluble solids. When the temperature rises above the gel point, the smaller

molecules become mobile and plasticize the micelles. The result is a colloidal solution known as the plastic state.

Berkowitz (38) also compares the plastic properties of coal with that of micellar polymers. He points out that polymeric substances acquire molecular mobility in stages; the various atomic groups of a single macromolecule attain additional degrees of freedom one by one as the temperature increases. Over certain temperature ranges, therefore, the mobility of such molecules is restricted to the two dimensions parallel to any supporting surface to which they happen to adhere. This two dimensional "liquid" layer functions in much the same way as does a boundary lubricant between two solid surfaces and enables the polymer (or coal) to undergo certain internal rearrangements under its own weight and thus to soften. Berkowitz believes that coals possess many features normally associated with polymers and that it is not unreasonable to assume that the softening of coal follows an analogous mechanism.

2.3.3 Mechanism of Swelling

The majority of authors consider swelling as a consequence of the softening of coal and the liberation of gas within the plastic coal material. This swelling is manifest in two forms -- the swelling of isolated coal particles and the swelling of coal particle agglomerates. Intraparticle swelling is believed to result from the formation of a fluid phase which obstructs the fissures and macropores through which evolved gases would otherwise escape. A gas pressure results that tends to deform the plastic mass by forming a bubble structure (2). Swelling of agglomerates is thought to occur in much the same way. Interparticle void spaces are filled

as a result of agglomeration of the fluid coal particles. This prevents the escape of gases, and the resulting gas pressure causes the plastic mass to intumesce or swell. VanKrevelen and co-workers (22) demonstrate the feasibility of such a mechanism by following the carbonization of a carefully prepared coal analogue.

According to the proposed mechanism, the extent of swelling must be a function of the rate of evolution of gas and of the plasticity. A certain minimum fluidity is necessary to prevent the escape of volatile products. However, once this fluidity is attained, the swelling will be greater the lower the plasticity or the higher the viscosity (2).

Berkowitz (39) considers swelling as a phenomenon almost independent of softening. He attributes swelling to the pressure of evolved gases forcing a path through the micropores of the coal. The greater the resistance to the passage of gas, the greater will be the pressure, and the greater will be the resultant swelling. According to this theory, the degree of swelling is determined by the internal pore structure of the starting coal. Berkowitz's theory rests upon a correlation between the swelling capacity of coals of different rank and internal surface measurements. This mechanism explains intraparticle swelling quite nicely but offers no account for interparticle swelling. The failure to explain swelling of agglomerates has led most authors to disregard this theory.

2.3.4 Resolidification

The mechanism of resolidification has already been touched on in connection with that of softening. All the theories, including the purely physical theories of softening, attribute the cause of

resolidification to a chemical reaction. They assume that the plastic phase undergoes thermal decomposition, giving rise to gaseous products which escape and a residue which is difficultly fusible or solid (2). The nature of this reaction is thought to be that of cracking reactions followed by condensation. The smaller molecules formed via cracking reactions comprise the volatile gases and tars and escape. The heavier fragments remain and are linked together by condensation-type reactions.

2.4 Oxidation Effects

Significant changes in the physical and chemical properties of coal occur upon mild oxidation. Qualitatively, the changes that take place are increases in weight, oxygen content, hygroscopicity, ignition temperature, and solubility in caustic solutions (resulting from an increase in humic acid content) and in alcohol, and decreases in carbon and hydrogen content, heating value, coking power, and average particle size (40).

2.4.1 Oxidation Kinetics

The extent to which the above changes take place depends on the duration of exposure to air and the rate of the oxidation reactions. The rate of the oxidation reactions is, therefore, of importance and should be considered accordingly. Several factors influence the oxidation kinetics of a coal, such as particle size, rank and petrographic composition of the coal, the temperature and time of oxidation, and the oxygen partial pressure and moisture content of the oxidizing medium (air).

2.4.1.1 Particle Size

Many investigators have held that oxidation of coal is entirely a surface phenomenon, because the rate of oxygen adsorption increases as the fineness of the coal particles increases (41). However, the work of Winmill (42) shows that the rate of oxidation is not simply proportional to the outer surface of the coal particles and that the total volume of oxygen adsorbed by a coal over a long period of time is independent of coal size. Oxidation, then, is not a simple surface action; but oxygen in some manner penetrates the coal particles. Oreshko states that oxidation rate is proportional to the "volume" of the coal and not to the external surface. The word "volume" implies specific volume and is related to porosity; it is not only the apparent surface of the coal grains that is involved but the pore or internal surface area as well (4). The important point is that for a given coal, smaller particle sizes will oxidize more rapidly. This is due to two factors; exposing greater external surface areas on grinding and providing easier access to the internal pore surfaces.

2.4.1.2 Rank and Petrographic Composition

In general, the lower the rank of the coal, the higher its oxygen and volatile matter contents, and the greater its susceptibility to attack by oxygen (4). Schmidt and Elder (43) have analyzed a series of coals covering the whole range of ordinary commercial coking coals. They show a threefold increase in characteristic rates of oxidation as initial oxygen content increases. If this study were enlarged to include noncoking coals, there would undoubtedly be a much larger range in the rates of oxidation. Carpenter and Giddings (44) studied several coals ranging in VM content from 5 to 32%. They

also show a progressive increase in oxidation rate with decrease in rank. However, their data exhibit a minimum in oxidation rate at a VM content of 6.2% (92% fixed carbon). This behavior is most likely due to the sharp increase in surface area observed for coals at around 90% carbon content (45).

Studies on rates of oxidation of petrographic constituents of coal have been limited to the four lithotypes identified by Stopes. Some authors report that these banded ingredients of coal should be listed according to their ease of oxidation as vitrain, clarain, durain and fusain (4). However, Stopes and Wheeler (46) and others (4) have measured the oxidation rates of the lithotypes also; and, they report the following order of decreasing rates: fusain, vitrain, clarain and durain.

Fusain would ordinarily be considered the most inert lithotype chemically and the most resistant to oxidation. The reason for the discrepancies between the reported relative ease of oxidation of fusain appear to lie in the fact that fusain is a very friable, charcoal like, constituent generally found as a fine powder or dust. Naturally occurring fusain usually has a high external surface area; and, therefore, one might expect an initially rapid rate of oxidation.

2.4.1.3 Temperature and Time Effects

Sevensler (47) conducted oxygen sorption studies on coals over the temperature range -183°C (liquid oxygen) to 92°C . He concludes that chemisorption of oxygen becomes appreciable even at temperatures of -5°C and that chemical reaction sets in at about 50°C and becomes an increasingly important factor at higher temperatures.

The rate at which coal adsorbs oxygen is greatly accelerated by a rise of temperature, but the increase in rate of oxygen adsorption for a given increase of temperature is not the same for all coals (41). For example, Graham and Jones (48) indicate that although some coals adsorb nearly three times as much oxygen at 60°C as at 30°C for a given period of time, other coals may adsorb nearly ten times as much at the higher temperature.

The results of oxidation rate studies are difficult to compare meaningfully because oxidation rates change dramatically with time (40). Initially, fresh, unoxidized, coal samples oxidize rapidly; this rate of oxidation decreases very sharply with time and finally approaches a more nearly constant value. Sevenster (49) looked at the kinetics of oxidation of several South African coals. He showed the typical initial high rate of adsorption, followed by a rapid decrease in oxidation rate, which became progressively smaller as saturation was approached. In fact, in the latter stages of the process, he noted temperature had only a small effect on the overall rate of adsorption. He assumed that chemisorption was the predominant (rate determining) process occurring during the early phase of adsorption and that the latter stages were dominated by transport processes. The data for the first stage of adsorption were fit to an Arrhenius expression and activation energies were calculated. The activation energies obtained ranged from 5 to 10 kcal/mole depending on the coal. These values were lower than Sevenster would have expected for chemical reactions involving bond breaking; and he was forced to accept that even at the early stages of oxidation, the effect of transport phenomena could not be neglected -- especially at reaction

temperatures above 50°C. Under these circumstances, the process is no longer simple and the determination of activation energies from Sevenster's rate data is not permissible. Sevenster concluded that one could not assume a homogeneous distribution of oxygen over the entire surface, even after some time, but must rather accept that the surfaces within larger pores were relatively densely populated while those in finer pores may have a very low concentration of adsorbed molecules.

Carpenter and Giddings (44) also studied the kinetics of oxidation of a series of coals. The range of coals used in their study was of higher rank than those used by Sevenster, so no direct comparison is feasible. For each coal and at each temperature studied, the authors identified three stages of oxidation. The initial stage was the most rapid in each case, and the subsequent stages showed progressively lower rates of oxygen consumption. An increase in temperature resulted in an increase in the rate of oxygen consumption in all three stages. The authors calculated activation energies for each of the three stages of oxidation. They suggested that chemisorption was the rate determining process throughout the observed extent of oxidation for several of the coals studied. The activation energies measured were of the order of 10 to 20 kcal/mole.

Various other authors have also fit oxidation data to Arrhenius expressions and have reported activation energies for the initial stage of oxidation (40). Even the highest of these values (~ 20 kcal/mole) are lower than those one would expect for chemical reactions where primary bonds are broken (50). As Sevenster (49) concludes, even at the early stages of oxidation, the effect of transport

phenomena cannot be neglected. Oxidation kinetics are complicated by diffusional processes, and the determination of activation energies from these rate data is often times of little fundamental meaning.

2.4.1.4 Oxygen Partial Pressure

For a given coal, oxidized under constant conditions of temperature, particle size and extent of oxidation, variation in the oxygen content of the oxidizing medium influences the rate of oxygen consumption in accordance with the following expression: $\text{Rate} = k P_{O_2}^n$, where rate is expressed as the weight of oxygen consumed per unit weight of coal per unit time, P_{O_2} is the oxygen partial pressure, n is the order of reaction with respect to oxygen and k is a rate constant (51).

The effect of oxygen partial pressure on rate has been investigated by a number of workers. Schmidt and Elder (43) have determined that the rate of oxidation at 99.3°C is proportional to P_{O_2} to the 0.61 power. Winmill (42) found a value of 0.5 for n at 30°C, and data obtained at 200°C show that the rate varies with the 0.71 power of oxygen concentration (40). Howard (50) has summarized the work of several authors and reports values of n that vary from 0.5 to 0.71. All of the experimental data available show that the rate is proportional to less than the first power of the oxygen concentration. There is some indication that the value of the exponent (n) increases with an increase in oxidation temperature.

2.4.1.5 Moisture

Moisture may act as a catalyst in the oxidation of coal, but experimental proof of such catalysis is difficult. Coal is so

complex and unstable that to remove all of its moisture without changing the composition is practically impossible (41). High-moisture coals oxidize more rapidly than low-moisture coals; however, this is not necessarily due to the water present. Coals of low rank usually have a high moisture content, and it is probable that the low rank itself is responsible for the higher oxidation rate (4). Most studies indicate that the effect of moisture is a function of coal type (41). Some coals adsorb oxygen more rapidly when dry and others more rapidly when moist. Low rank coals appear to adsorb oxygen more slowly from moist air than from dry air, but the reverse is true of higher rank coal. Other studies (40) indicate that the effect of moisture is very slight.

While moisture may or may not alter the rate of oxygen addition to coal, there is good reason to believe that water will react with the coal during its oxidation. Smith and coworkers (52) studied the interaction of water with clean carbon surfaces in the temperature range 25-200°C. The reaction of water with carbon gives hydrogen gas and a carbon-oxygen complex. They suggest that the stable complex may contain hydroxyl groups which can be desorbed as water at higher temperature. Surface impurities such as sulfur and oxygen (readily found in coal) were shown to increase the reactivity to water enormously. Studebaker (53) points out that oxidation of carbons in the presence of moisture leads to surface peroxide formation and that moisture is essential for peroxide formation. Some evidence does exist for peroxide formation during the oxidation of coal (4,54,55). These points will be discussed further in the next section dealing with the mechanisms of coal oxidation.

2.4.2 Mechanism of Oxidation

To date, the exact nature of the uptake of oxygen by coal has not been completely elucidated. The fact that coal is a solid of complicated and undefined chemical structure causes many difficulties in explaining the details of the process. Schmidt (40) suggests the following mechanism for the oxidation reaction:

The first step in this mechanism involves physical adsorption of oxygen on coal. However, little evidence exists to support this first step. Sevenster (47) has shown that chemisorption of oxygen on coal predominates at temperatures as low as -5°C and that the amount of reversibly adsorbed oxygen above 50°C is negligible. It appears that, at best, only a small fraction of the total oxygen adsorbed is held physically. An alternative explanation to this first step, and one which is finding increasingly more support, is that the initial oxidation is due to peroxide formation. Evidence for the peroxidic groups in oxidized coals has been shown by several investigators. Yohe and coworkers (4) demonstrated the oxidizing power of weathered coals and were able to show that fresh coal (unoxidized) was devoid of oxidizing action. Jones and Townend (54) suggest a similarity between the mechanism of oxidation of coal and that of the oxidative processes undergone by oils, rubber and food-stuffs. In these processes, formation of endothermic complexes (possibly hydroperoxides) plays an important role. Both Jones and Townend (54) and Chakravarty (55) have followed the formation of

peroxidic-groups during the oxidation of coal, and they discuss the importance of "peroxygen" groups in the oxidation process. These authors state that moisture is essential for adsorption and formation of peroxidic groups. It is likely that this requirement is met by the inherent moisture of the coal, in light of the fact that high moisture coals generally oxidize more rapidly than low moisture coals.

Peroxygen-complexes are relatively stable at lower temperatures, and the second step in the oxidation mechanism is extremely slow. Above a temperature of about 70°C, however, the peroxygen becomes unstable and decomposes to yield stable coal-oxygen complexes with the evolution of CO₂, CO and H₂O. VanKrevelen (12) shows these stable complexes to be present in the form of carboxyl, hydroxyl, carbonyl and ether and heterocyclic oxygen groups. Carboxyl and ether and heterocyclic oxygen groups predominate while hydroxyl is found in about half the concentration of carboxyl. This increase in acid groups on the coal surface results in the formation of humic acids, as is evidenced by the fact that many coals on mild oxidation readily yield significant amounts of alkali-soluble material (4).

The oxygen-complexes formed during the second stage of oxidation are very stable at temperatures below the ignition point of the coal, and further oxidation at these temperatures is slow. At temperatures above the ignition point, the final step of the oxidation mechanism comes into play. The surface complexes become increasingly unstable, breaking down to yield CO₂, CO and H₂O.

2.4.3 Effects on Plastic Properties

The plastic properties of coking coals are very markedly modified by oxidation, even slight oxidation. Changes in these properties

are often observed before any change in the proximate and ultimate analyses can be detected; and, at detectable levels, oxidized coals may not exhibit any softening or swelling tendencies (2). Many studies of the changes in coking properties upon oxidation have been conducted over the past fifty years. In general, the results of these studies show that the coking power of a coal is progressively destroyed by oxidation.

Marshall and coworkers (56) examined the changes in agglutinating power of coals due to exposure to air at room temperature. Their tests show clearly that there is a definite and continual reduction in agglutinating value as a coal is oxidized. They conclude that the agglutinating test may be conveniently used as a sensitive method to detect and follow oxidation in a coal. In this study, the authors did not measure the level of oxidation directly. They compared the changes in agglutinating power as a function of time of exposure to air.

In a similar study, Rose and Sebastian (57) oxidized several coals for varying periods of time at 80°C. They note that in some coals the agglutinating value drops to zero within a short time (9 days). Other coals show little change in agglutinating value during the first week of oxidation, after which it falls at a rapid and regular rate until a zero value is reached. Still other coals show an initial increase in agglutinating value, and it is not until some time later that the value has again dropped as low as the original coal. Even with these coals the value falls to zero after longer periods of oxidation. The authors conclude that there is not only a lack of direct correlation between the agglutinating value and oxygen

content of oxidized coals but that most of the increase in oxygen content occurs without much accompanying change in agglutinating value. Also, while the drops in agglutinating value take place, the oxygen content (ultimate analysis) shows little change.

Schmidt, Elder and Davis (58,59) examined the effects of oxidation on several carbonizing properties. They found that the majority of coals tested showed serious impairment of coking power before they were oxidized enough to decrease the heating value by one percent and before their ultimate and proximate analyses showed changes definitely greater than the experimental error of analysis. Their results show that on carbonization the yield of tars decreases rapidly due to oxidation. This decrease in the yield of tars is paralleled closely by an increase in the yield of coke produced. The authors state that the decrease in tar yield is the most sensitive carbonizing property for indicating the extent of oxidation of a coal. They also found that oxidation increased the apparent specific gravity of the coke formed and, in the coals studied, that the coke strength increased slightly up to a certain critical value and then decreased rapidly with further oxidation. The agglutinating values for these oxidized coals followed the same pattern as coke strength.

Davis et. al. (60) also studied several carbonization properties of some coking coals. Their results agree with those of Schmidt and coworkers (58,59). In addition, they examined the changes in coal fluidity as measured in both the Gieseler and Davis plastometers. They report that the principal effect of oxidation is to lower the maximum fluidity and to increase the softening or fusion temperature. They also report a reduction in the resolidification temperature.

Russell and Perch (61) also have studied the changes in fluidity as measured in the Gieseler plastometer. Their results show that the most dramatic reduction in maximum fluidity occurs in the early stages of oxidation, after which the sensitivity to oxidation is markedly decreased.

In other studies, Kreulen (62) has shown that the B.S. swelling number may at first increase on mild oxidation for certain coals but in general, that swelling number decreases progressively with extent of oxidation. Boyer (63) has also observed an increase in swelling of some coals as measured by dilatometry. This initial increase is followed by a rapid decrease in swelling on further oxidation. Ignasiak, Nandi and Montgomery (64) note that the decrease in dilation is a very sensitive indicator of the degree of oxidation for coals which possess high swelling properties. However, they find that dilation properties cannot be used successfully for detecting the extent of oxidation of a coal which itself has small dilation in the fresh unoxidized state. Kam, Hixson and Perlmutter (65) have studied oxidation effects using a Foxwell-type test apparatus. Their results show an increase in softening temperature on oxidation and a progressive loss in fluidity. They note that for a given level of oxidation, the effectiveness of oxygen in reducing coking properties increases as the particle size of the coal decreases.

2.4.4 Causes of Reduction in Coking Power

It is generally thought that the loss in plastic properties of coking coals upon oxidation is due to the introduction of oxygen crosslinks into the coal. An analogy can be drawn with coal and certain polymer systems. In the latter, introduction of relatively

few crosslinks (one every 40-50 main chain atoms) reduces the mobility of polymer chains to the point that a previously thermoplastic polymer becomes rigid and can no longer attain a plastic state (66). The exact nature of the oxygen crosslinks believed to be responsible for losses in plastic properties is still under speculation, and several papers have been published on the topic in recent years.

Ignasiak, Clugston and Montgomery (67) propose that oxygen crosslinks are formed via condensation reactions between acid hydroxyl groups found in oxidized coals. They note that oxidation brings about an increase in the reactive oxygen groups; $-OH$, $-COOH$ and $>C=O$. They believe that as the temperature is elevated (on carbonization) the acid hydroxyl groups undergo condensation reactions to yield ether-type crosslinks with the liberation of water. From $^{18}O_2$ tracer studies they infer that only about 12% of the total labelled oxygen adsorbed during oxidation is responsible for the loss of dilation resulting from ether bonds.

Ignasiak, Szladow and Montgomery (68) provided further evidence to support the above hypothesis. They reasoned that if they could prevent acid hydroxyl groups from crosslinking, then they could restore the plastic properties of an oxidized coal. They used an ion exchange treatment to replace the proton sites of phenolic and carboxylic groups in oxidized coal with barium ions. This treatment was successful in blocking the acid hydroxyls, and the exchanged coals exhibited almost complete restoration of swelling and fluid properties as measured by a Ruhr dilatometer and a Gieseler plastometer. Their results also suggest that carboxyl groups are not responsible for changes in plasticity, and they conclude that only the

more strongly acidic hydroxyl groups have a marked effect on the plasticity and dilation. The authors emphasize that the deterioration of coal fluidity and dilation is due to only a small fraction of the oxygen added. A very small amount of oxygen (0.01-0.02% by wt. coal) is responsible for substantial changes in fluidity. Heat treatment studies were also carried out which led to the conclusion that the condensation reactions responsible for the reduction of the dilation of slightly oxidized coal do not proceed below 380°C.

In contrast to the above statement, Wachowska, Nandi and Montgomery (69) present evidence to suggest that decreases in dilation of oxidized coals may be explained by the formation of non-reactive oxygen linkages during the low-temperature oxidation of coals. These linkages, possibly ether-type, are considered to result from the thermal decomposition of peroxides and hydroxyl groups at temperatures of the order of 85 to 100°C. This assumption is based on the fact that the authors could not significantly improve the plastic properties of oxidized coals by removal or blocking of peroxide, keto, aldehyde and hydroxyl groups.

In this same study, Wachowska et. al. (69) and in a later study Wachowska and Pawlak (70) treated oxidized coals with naphthalene anion in tetrahydrofuran. This treatment is known to cleave diaryl and aryl-alkyl ether bonds (71). They found that cleavage of these ether linkages led to a lowering of the "melting point" and, in some cases, to a large increase in dilation and a substantial increase in Gieseler fluidity. These results provide further evidence that ether-type crosslinks are responsible for losses in plastic properties on oxidation. Wachowska, Nandi and Montgomery also showed that following

this treatment a long drying period at elevated temperature (70°C) led to a reduction in dilation. The drying was carried out under vacuum; and so it can be concluded, as suggested previously, that cross-linking reactions do occur at temperatures as low as 70°C. In this experiment, the authors were able to reduce the loss in dilation on drying by blocking acid hydroxyl groups with barium. However, even after the ion exchange a substantial decrease in dilation still occurred on drying.

The work of Wachowska and coworkers (69,70) does not necessarily negate the work of Ignasiak et. al. (68). In the former study (Ignasiak), the coals used had been only slightly oxidized; and the authors emphasize that the deterioration of coal fluidity and dilation is due to a very small fraction of the oxygen added. In Wachowska's studies, the coals were much more severely oxidized. The combined studies suggest that crosslinking reactions may indeed occur at lower temperatures but that these reactions proceed slowly.

Painter et. al. (72) have used Fourier transform infrared spectroscopy to characterize a high volatile coking coal which had been weathered to various levels of oxidation. Through the use of this technique, they were able to identify ester-type oxygen linkages in the weathered coal. However, no ether-type oxygen was observed. The authors hypothesize that ester crosslinks in the oxidized coals may be responsible for losses in swelling upon oxidation. Their results indicate that ester groups are not formed initially, but become evident at later stages in the oxidation process. In a follow-up to this study (73), samples of an HVA coal were oxidized at elevated temperatures to various levels of weight gain. The FTIR studies of these

oxidized coals indicate that in the early stages of oxidation the main oxygen containing functional groups formed are carbonyl and carboxyl. At higher degrees of oxidation, there is evidence of a significant increase in ether, ester and phenolic groups. It appears from these results that losses in swelling and fluid properties may be attributed to the formation of both ether- and ester-type cross-links.

3. STATEMENT OF THE PROBLEM

This study is an attempt to quantify the swelling and softening properties of selected coals and to monitor the changes in these properties upon mild oxidation. From the review of the literature, one notes that, in the past, most studies of coking properties had been directed at determining the behavior of coals in the coke oven and that the results of such studies were analyzed only from the standpoint of the quality of the coke produced. Many of the test methods used in these studies were designed to yield a single number or index which, hopefully, would reflect the coking potential of the coal. This study has been directed at gaining a more fundamental understanding of coking phenomena; and, consequently, most of the established test methods used by the coking industry were not of much use. For this study, two types of test methods, which might prove useful, came to mind. They are dilatometer and plastometer test methods. Both of these techniques have been shown to provide several characteristic parameters for study, and they supply detailed information on the plastic transitions occurring in coal during heat treatment.

A primary objective of this study was to establish a satisfactory method of quantifying swelling and softening properties of caking coals. To this end, it was decided to investigate the applicability of a DuPont 942-TMA (Thermomechanical Analyzer) dilatometer unit. The DuPont 942-TMA is a very sensitive dilatometer system, which offers a high degree of flexibility with regard to selection of coking variables. Therefore, it was thought that this apparatus might prove useful in the analysis of coking properties. The first step in this

investigation then was to determine the utility of the 942-TMA system in the analysis of caking properties. A study was designed, therefore, to determine the effects of TMA variables on the coking parameters measured with the dilatometer. From the results of this study, the capabilities of the 942-TMA were assessed and standard dilatometer operating conditions were adopted.

Following the successful completion of this first phase, the remaining goals in this study involved using the TMA system to analyze a series of caking coals and to study changes occurring in swelling and softening properties upon oxidation. These studies should lead to a better understanding of the coking mechanism, in general, and of the subsequent effects of oxidation on this mechanism, in particular. This type of information is essential if one wishes to fully utilize the vast reserves of caking coals found in this country.

4. EXPERIMENTAL

4.1 Thermomechanical Studies

In this study it was decided to investigate the applicability of a DuPont 942-TMA (Thermomechanical Analyzer) dilatometer system for the characterization of the swelling and softening properties of caking coals. The DuPont 942-TMA is a highly sensitive microdilator-metric system equipped with a derivative computer (Figure 1). The heart of the TMA is a movable-core, linear variable differential transformer (LVDT). It provides a DC output proportional to the linear displacement of its core. The transformer core is incorporated in the dilatometer probe. Thus, the position of the probe determines the voltage induced in the secondary windings of the transformer. This voltage is then displayed on a DuPont 990-Thermal Analyzer recorder. In addition, the derivative of the voltage is determined by an electronic derivative circuit and is also recorded on the 990-recorder.

The sample and the base of the dilatometer probe are surrounded by a cylindrical silver core heater, containing a Platinel-II control thermocouple. This heater is controlled by a DuPont 990-Temperature Programmer Controller. A sample thermocouple is attached to the sample holder tube and provides an output proportional to the sample temperature. This temperature is recorded on the T-axis (x-axis) of the 990-recorder. The system is also provided with a gas inlet tube so that samples can be flushed with inert gas (N_2) to avoid oxidation during heat up.

Figure 1. SCHEMATIC OF 942-TMA UNIT

4.1.1 Determination of Dilatometer Test Conditions

Before using the 942-TMA to characterize a series of coals and to study oxidation effects, it was first necessary to establish a standard set of operating conditions. A coal was selected from The Pennsylvania State University/Department of Energy Coal Data Base, and a series of experiments were conducted to determine the effects of dilatometer variables on dilation parameters.

4.1.1.1 Selection of a Sample

The coal selected for this preliminary study was PSOC-337. This was a high swelling, high volatile A bituminous coal from the Lower Kittanning Seam in Pennsylvania. The selection criteria were a high free swelling index, high vitrinite content and low ash content. Selecting a coal of high vitrinite content was necessary to avoid the anomalous behavior often observed for coals of high exinite or high inertinite content (2). Low ash content was also important since inert material does not contribute to dilation and, when in high enough concentrations, actually inhibits swelling (3,9). Finally, the coal selected had high swelling characteristics so that the transitions observed during heating would be more pronounced. Table 1 contains the proximate, ultimate and maceral analyses data received from the PSU Coal Research Section for PSOC-337.

4.1.1.2 Sample History

A ten pound sample of PSOC-337 was obtained from The Pennsylvania State University Coal Research Section. The sample had been ground to minus 1/4 in. and was sealed in a container in a N₂ atmosphere. Upon receipt of this sample, the coal was ground to pass a 30 mesh screen (U.S. Standard sieve), split into several fractions by riffing,

TABLE 1

Analyses Determined for PSOC-337, HVA Coal from
the Lower Kittanning Seam, Pennsylvania

Proximate Analysis	As Received	Dry Basis	Ultimate Analysis:	Dry Ash Free Basis
% Moisture	2.28	-	% C	84.85
% Ash	8.32	8.51	% H	5.80
% Volatile Matter	34.19	34.99	% N	1.58
% Fixed Carbon	55.21	56.50	% S	1.62
			% O (by diff.)	6.14

Calorific Value (dry basis) = 13,884 BTU/lb

Free Swelling Index = 8

Reflectance Rank = HVA

Maceral Composition	DMMF (Vol. %)		
Vitrinite	74.0	}	Total Vitrinites 75.1
Pseudo-Vitrinite	1.1		
Fusinite	1.8	}	Total Inertinites 8.4
Semi-Fusinite	2.8		
Macrinite	1.4		
Micrinite	2.4		
Sporinite	14.3	}	Total Exinites 16.4
Resinite	2.0		
Alginite	0.1		

and stored in bottles. Due to the nature of this study, it was imperative that samples be kept free from oxygen whenever possible. Therefore, all grinding and sieving procedures were carried out in glove bags under a N_2 atmosphere. Samples were then stored in desiccators under N_2 .

Free swelling index (FSI) measurements were carried out as a check for possible oxidation of PSOC-337 during storage at the Coal Research Section. Measurements were conducted in a BCR developed, electrically-heated FSI test unit. The procedure followed conformed to the ASTM Standard Method of Test Designation D720-67 (8). An FSI of 8.0 was measured for this sample. The original value reported for this coal was also 8.0; therefore no detectable oxidation had occurred prior to receipt of this sample.

4.1.1.3 TMA Test Variables

The purpose of the preliminary study was to determine the effects of TMA variables on the measured dilation parameters. The TMA variables studied were heating rate, coal particle size, and external load.

Three heating programs were selected for study; $3^\circ\text{C}/\text{min}$, $20^\circ\text{C}/\text{min}$ and $50^\circ\text{C}/\text{min}$. A $50^\circ\text{C}/\text{min}$ program was the maximum controlled heating rate attainable with the apparatus. The $3^\circ\text{C}/\text{min}$ heating program was chosen as a basis for comparison with standard dilatometer methods as used in the coke industry (2). A $20^\circ\text{C}/\text{min}$ rate was selected as an intermediate program.

Four particle size ranges were selected for study (see Table 2). The oxidation rate of a coal sample has been shown to be particularly sensitive to particle size (4,41,42). For this reason it was necessary

TABLE 2

Selected Properties of Sieve Fractions Chosen for Study

Sieve Fraction U.S. Standard Sieve	Particle Diameter Range μm	% Moisture After Storage in Dry N_2	% Ash Dry Basis
-40 x +60 mesh	< 425 > 250	1.7	8.4
-100 x +150 mesh	< 150 > 106	2.1	8.5
-200 x +230 mesh	< 75 > 63	2.6	8.7
-200 mesh	< 75	2.3	8.5

to select narrow particle size ranges for the oxidation segment of this work.

External pressure exerted on the coal sample via the dilatometer probe was also expected to have some effect on dilation parameters (3). Therefore, three load modes were selected for study -- 5g (17.7 g/cm^2), 1g (3.5 g/cm^2), and no apparent load. The numbers in parenthesis represent the force applied per unit surface area of the dilatometer probe.

4.1.1.4 Sample Preparation

Some concern was expressed over the possibility of maceral and mineral segregation on grinding and sieving. Therefore, to keep segregation effects to a minimum, a careful grinding and sieving procedure was adopted. A sample of minus 30 mesh coal (see 4.1.1.2) was obtained by riffing. This sample was ground by hand with a mortar and pestal in a glove bag under a N_2 atmosphere. To reduce the formation of fines, grinding was done for intervals no longer than 60 sec at one time, followed by sieving. Grinding and sieving were continued until the entire sample was ground to minus 40 mesh. The minus 40 mesh coal was then split into four equal proportions by riffing. The 40 by 60 mesh fraction of one of these samples was collected and stored, and the minus 60 mesh coal was discarded. The remaining three minus 40 mesh samples were recombined; and, following the same procedure as above, this coal was ground entirely to minus 100 mesh. The 100 mesh coal was quartered by riffing and the 100 x 150 mesh portion of one of the fractions was collected and stored. The remaining fractions were recombined, and the same procedure was followed to

obtain a 200 x 230 mesh coal fraction and a -200 mesh coal sample. Moisture and ash measurements were then made on each of the four sieve fractions collected (Table 2) in accordance with ASTM standard procedures (74,75). These procedures were altered slightly in that the coal samples were sized instead of using minus 60 mesh coal as specified in the standard for moisture determination. Also, samples were stored under dry N_2 prior to the moisture and ash determinations. Little variation in ash and moisture content with particle size was found. These data show that segregation effects have been minimized through the use of the grinding and sieving procedures described above.

4.1.2 Dilatometer Procedure

Samples for dilatometer experiments were prepared in quartz sample vials provided with the TMA unit. First, a clean sample vial was centered directly beneath the dilatometer probe. The probe was lowered, taking care that the movement of the dilatometer was not restricted by contact with the side walls of the vial, to within a few thousandths of an inch above the vial bottom. This was determined from the transducer output on the recorder. A one gram weight was then placed on top of the probe, so that the dilatometer rested flush upon the bottom of the vial. The transducer was then adjusted for zero output on the recorder.

Next the one gram weight was removed and the probe was raised slowly to a position above the top of the vial. The vial was removed and weighed (W_v), and then a coal sample was added to it*. This sample

* It had been determined experimentally that the maximum sample size which could be used for a high swelling coal such as PSOC-337, was 20 mg.

was levelled by gently tapping the vial and then packed. The packing procedure involved pressing firmly on top of the sample with a tamping rod (provided with the dilatometer unit), rotating the vial 90°, and then pressing firmly on top of the sample again and rotating 90°. This procedure was repeated a total of twelve times.

After packing the sample, the vial was again weighed (W_{VS}). It was then centered under the dilatometer probe and the probe was lowered to within a few thousandths of an inch above the sample. The one gram weight was placed on top of the probe so that the dilatometer rested flat upon the sample. The height of the coal sample (h_c) was then determined by the displacement of the probe from the zero position.

Following the above procedure, the sample holder cell was flushed with a stream of N_2^* gas (300 cc/min at 25°C), which was scrubbed of O_2 by passing over copper turnings heated at 500°C. While the sample was being purged with N_2 , the TMA running conditions were set. The proper load weight was placed on the dilatometer probe, and the transducer was reset for zero output. The heating program was then selected, and the heater assembly was fit into place around the sample holder. An insulating Dewar was attached around the heater. The system was purged with N_2 for 15 minutes before the heating program was started. Heating programs of 20°C/min and 50°C/min were run from ambient up to 650°C. Heating programs of 3°C/min were executed by heating rapidly to 250°C followed by controlled heating at 3°C/min from 250°C to 600°C.

4.1.3 Dilation Parameters Measured

Figure 2 is an example of a typical dilatometer experimental run for PSOC-337. Careful examination of this figure shows that much

*The N_2 used in this work was research grade, prepared by Air Products Co.

Figure 2. TYPICAL TMA OUTPUT FOR PSOC-337 (HVA COAL)
50 $^{\circ}$ C/min Heating Rate, 1g Dilatometer Load,
200 x 230 Mesh Coal

quantitative information about the softening and swelling of coal samples can be obtained with the DuPont 942-TMA apparatus. The parameters defined by the dilatometer trace and selected for study in this work were:

- i) The onset of softening temperature (T_s)--this was the temperature at which softening and plastic deformation of the coal sample became evident. It was clearly defined as the temperature at which the derivative trace crossed the baseline (A').
- ii) The initial dilation or fusion temperature (T_d)--this temperature was also defined by the derivative trace (B') and represented the temperature at which swelling of the coal commenced.
- iii) The resolidification temperature (T_r)--this temperature was determined from the dilatometer trace (C) and corresponded to the point at which plastic behavior of the coal was no longer evident.
- iv) The maximum expansion temperature (T_e)--this temperature was determined from the dilatometer trace (E) and corresponded to the point at which maximum expansion of the coal sample was recorded.
- v) The initial contraction--this was defined as the vertical distance between the probe position at maximum contraction and at the zero position (D). The zero position was taken as the baseline corrected for normal thermal expansion of the coal.

- vi) The maximum expansion--this was defined as the vertical distance between the probe position at maximum expansion and the corrected baseline (E).
- vii) The final contraction--this was determined by the vertical distance between the probe position at maximum expansion and at the temperature of resolidification (F).
- viii) The total dilation--this was defined as the vertical distance between the probe position at maximum expansion and at maximum contraction (E + D).

It should be noted that the derivative trace in Figure 2 is off-set by about 5°C along the temperature-axis. Therefore, although B and B' do not occur at the same position on the T-axis, they do represent the same temperature.

Over the temperature region in which dilation occurs (B-E), one observes large oscillations in the experimental trace. This is due to the rapid evolution of volatiles through the plastic coal mass. This gives an indication of the high degree of fluidity attained by the coal during heat treatment. This rapid oscillation of the dilatometer probe results in the derivative trace moving off-scale; and, therefore, the derivative is no longer useful in this region.

4.1.4 Calculations

Contraction and expansion data were reported on a percent volume change basis. The vertical probe displacement values were converted to volume changes using the following equation:

$$\% \text{ Volume Contraction} = \frac{D}{X_C W_S} 100 \quad (1)$$

where D is equal to the vertical displacement of the probe on

contraction; W_s is the weight of the sample; and X_c is a volume conversion factor. X_c values were determined as average values calculated from h_c and W_s data as determined in the procedure outlined in Section 4.1.2. Assuming the sample vials to be perfect cylinders:

$$X_c = \frac{h_c}{W_s} \quad (2)$$

Ninety-five percent confidence values for X_c typically showed a reproducibility of $\pm 2-3\%$.

Similarly:

$$\% \text{ Volume Expansion} = \frac{E}{X_c W_s} 100 \quad (3)$$

and:

$$\% \text{ Volume Final Contraction} = \frac{F}{X_c W_s} 100 \quad (4)$$

4.1.5 Standardization of the TMA Technique

A preliminary study was conducted to determine the optimum TMA operating conditions. The effects of the TMA variables discussed above (4.1.1.3) on the measured dilation parameters (4.1.3) were investigated. Over 260 TMA experiments were carried out and standard TMA operating procedures were established. The results of this work are found in Chapter 5.1.

4.2 Studies on Raw Coals

4.2.1 Selection of Samples

Several coal channel samples and their corresponding lithotypes were selected for study with the 942-TMA dilatometer system. These samples varied in rank (as determined by maximum vitrinite reflectance) from HVC to LV bituminous (76) and were chosen as being representative of the range of caking coals. In all, a total of nineteen samples

were examined in this investigation. The proximate, ultimate and maceral analyses data for these coals, received from the PSU Coal Research Section are listed in Tables 3 through 5.

4.2.2 Sample History and Preparation

All of the coals used in this study were freshly collected samples. These coals were received as minus 20 mesh in cans sealed under N_2 . Immediately upon receipt of these samples, they were split by riffing and stored in bottles under N_2 . Samples were then ground to minus 200 mesh following the procedure outlined in Section 4.1.1.4. Grinding and sieving procedures were conducted in glove bags under a N_2 atmosphere to prevent oxidation. In the work carried out on PSOC-337, there was some evidence of possible oxidation of minus 200 mesh samples after prolonged storage (two months) under N_2 (Section 5.1.4). For this reason, all dilatometer work was conducted on these samples within 12 hr of grinding to minus 20 mesh.

4.2.3 Dilatometer Procedure

Minus 200 mesh coal samples were prepared according to the procedure outlined in Section 4.1.2. The standard dilatometer operating conditions established for this work involved operating at a 50°C/min heating rate under a 1g dilatometer load. A total of five experimental runs were conducted for each sample under these conditions. Dilation parameters were reported as 95% confidence values determined from the five runs.

TABLE 3
Proximate Analyses of Raw Coals

Sample PSOC	Rank	As Received				Dry Ash Free		F.S.I.
		Moisture (%)	Ash (%)	Volatile (%)	Fixed Carbon (%)	Volatile (%)	Fixed Carbon (%)	
1082	HVC	8.51	15.01	33.48	43.00	43.78	56.22	1 1/2
1083	HVC	8.56	6.66	36.72	48.66	43.31	57.39	3 1/2
1099	HVA	1.77	11.15	33.65	53.43	38.64	61.36	8 1/2
1100	HVA	1.72	9.36	36.05	52.87	40.54	59.46	8
1101	HVA	1.95	5.32	35.43	57.30	38.21	61.79	8
1102	HVA	1.91	7.57	34.52	56.00	38.14	61.86	8
1103	HVA	2.00	4.64	40.11	53.25	42.96	57.04	6 1/2
1104	HVA	1.95	3.36	41.50	53.19	43.83	56.17	6 1/2
1105	HVA	1.93	3.73	39.91	54.43	42.30	57.70	6 1/2
1106	HVA	1.77	4.25	38.99	54.99	41.49	58.51	6 1/2
1112	HVB	4.73	6.61	41.53	47.13	46.84	53.16	3
1113	HVB	4.35	7.73	33.53	54.39	38.14	61.86	2 1/2
1114	HVB	4.43	5.65	43.31	46.61	48.17	51.83	2 1/2
1115	HVB	5.02	5.18	42.46	47.34	47.28	52.72	3
1116	HVA	3.07	6.62	37.83	52.48	41.89	58.11	6
1117	HVA	1.95	6.96	38.17	52.92	41.90	58.10	6

TABLE 3 (Continued)

Sample PSOC	Rank	Moisture (%)	As Received			Dry Ash Free		F.S.I.
			Ash (%)	Volatile (%)	Fixed Carbon (%)	Volatile (%)	Fixed Carbon (%)	
1118	HVA	2.87	18.89	39.17	39.07	50.06	49.94	4 1/2
1119	HVA	1.58	6.63	40.11	51.68	43.70	56.30	4 1/2
1133	LV	0.91	19.00	19.04	61.05	23.77	76.23	---

TABLE 4
Ultimate Analyses of Raw Coals

Sample PSCC	Dry Ash Free Basis (% by wt.)					
	Carbon	Hydrogen	Nitrogen	Chlorine	Sulfur	Oxygen
10E2	75.60	5.49	1.56	0.05	7.13	10.18
10E3	79.37	5.54	1.31	0.03	3.52	10.24
10E9	83.86	5.67	1.53	0.16	1.53	7.24
11C0	84.59	5.76	1.54	0.11	1.30	6.70
11C1	84.93	5.74	1.59	0.13	0.75	6.86
11C2	84.20	5.46	1.72	0.17	1.89	6.56
11C3	83.11	5.63	1.46	0.14	2.00	7.66
11C4	84.47	5.65	1.46	0.12	1.85	6.43
11C5	83.50	6.57	1.58	0.12	2.37	6.66
11C6	84.80	5.54	1.48	0.10	1.42	6.65
11I2	80.57	5.87	1.32	0.03	0.70	11.51
11I3	78.48	6.05	1.26	0.01	0.79	13.39
11I4	80.78	6.10	1.33	0.01	0.49	11.29
11I5	81.40	5.85	1.36	0.02	0.54	10.82
11I6	82.91	5.53	1.60	0.11	0.59	9.21
11I7	82.70	5.79	1.65	0.10	0.59	9.17

TABLE 4 (Continued)

Sample PSOC	Dry Ash Free Basis (% by wt.)					
	Carbon	Hydrogen	Nitrogen	Chlorine	Sulfur	Oxygen
1118	78.86	4.63	1.37	0.09	0.46	14.60
1119	83.24	5.70	1.62	0.12	0.63	8.69
1133	87.60	5.16	1.39	0.09	2.00	3.76

TABLE 5
 Maceral Compositions of Raw Coals

Sample PSOC-	Vitrinite Reflectance	Vitrinite	Pseudo- Vitrinite	Exinite	Resinite
1082	0.57	89.6	0.0	2.1	0.0
1083	0.58	93.3	0.3	1.3	0.1
1099	0.89	86.4	1.0	1.4	0.0
1100	0.88	77.5	0.8	5.1	0.0
1101	0.90	83.6	1.7	1.6	0.2
1102	0.89	82.4	3.1	1.8	0.2
1103	0.80	62.2	6.5	10.6	0.4
1104	0.77	71.5	8.2	6.4	0.2
1105	0.79	65.3	4.9	10.5	0.2
1106	0.84	48.9	4.2	14.4	0.3
1112	0.62	80.5	2.2	2.7	0.4
1113	0.59	80.0	2.3	1.9	0.2
1114	0.56	83.1	0.0	2.6	0.1
1115	0.57	85.1	1.9	1.8	0.2
1116	0.77	84.2	1.9	1.3	0.5
1117	0.78	87.0	2.8	1.4	0.0
1118	0.86	80.2	3.5	1.0	0.4
1119	0.76	82.3	4.5	2.7	0.3
1133	1.55	88.7	0.0	0.0	0.0

TABLE 5. (Continued)

Sample PSOC-	Fusinite	Semi- Fusinite	Macrinite	Micrinite	Seam
1082	2.9	3.6	0.0	1.8	Kentucky #11
1083	1.9	1.7	1.0	1.3	Kentucky #11
1099	3.6	6.2	0.3	1.1	Pittsburgh
1100	3.0	9.6	1.0	3.0	Upper Lithotype
1101	4.1	6.2	0.5	2.1	Middle Lithotype
1102	3.1	6.9	0.2	2.3	Bottom Lithotype
1103	1.4	11.6	0.7	6.6	Elkhorn #3 Kentucky
1104	2.5	5.1	0.2	5.9	Upper Lithotype
1105	2.3	10.3	0.6	5.9	Middle Lithotype
1106	2.3	21.3	0.5	8.1	Bottom Lithotype
1112	2.4	10.2	0.7	0.9	Blind Canyon Utah
1113	2.0	11.3	0.2	2.1	Upper Lithotype
1114	1.7	11.1	0.6	0.8	Middle Lithotype
1115	2.8	5.7	0.2	2.2	Bottom Lithotype
1116	3.0	7.5	0.7	0.9	Upper Sunnyside Utah
1117	2.7	5.6	0.1	0.4	Upper Lithotype
1118	4.3	9.4	0.3	0.9	Middle Lithotype
1119	1.2	7.2	0.5	1.3	Bottom Lithotype
1133	1.1	6.2	0.4	3.6	Lower Kittanning, Pa.

4.3 Oxidation Studies

4.3.1 Sample Selection, History and Preparation

Two coals were selected for the oxidation segment of this study. They were PSOC-1099, a high volatile A bituminous coal from the Pittsburgh seam in Pennsylvania, and PSOC-1133, a low volatile bituminous coal from the Lower Kittanning seam in Pennsylvania.

These samples were collected fresh, and were received as minus 1/4 inch in cans sealed under N_2 . Upon receipt of these samples, they were ground to pass a 30 mesh screen, split into several fractions and stored according to the procedure outlined in Section 4.1.1.2. To minimize maceral and mineral segregation on grinding and sieving, sieve fractions (40 x 60 mesh and 200 x 230 mesh) were prepared for study according to the procedure outlined in Section 4.1.1.4. Proximate, ultimate and maceral analyses data for the raw coals can be found in Tables 3 through 5. In addition, separate maceral analyses, moisture and ash determinations were carried out on each of the sieve fractions used in the oxidation studies. These data are given in Tables 6 and 7. Comparison of the data in Tables 6 and 7 with that for the corresponding raw coals in Tables 3 and 5 show that some maceral and mineral segregation on grinding and sieving is apparent. However, this segregation appears to be slight.

4.3.2 Preoxidation Procedure

4.3.2.1 Apparatus

Samples were oxidized in a Fisher Thermo Gravimetric Analyzer (TGA) System, Series 300 (Figure 3). This system is composed of a Cahn RG Electrobalance which is capable of continuously monitoring

TABLE 6
Maceral Compositions of Sieve Fractions

Coal PSOC-	Sieve Fraction	Maceral Data							
		Vitrinite	Pseudo- Vitrinite	Fusinite	Semi- Fusinite	Macrinite	Micrinite	Exinite	Resinite
1099	40x60	80.3	1.9	3.3	7.7	0.8	2.4	3.5	0.1
1099	200x230	87.9	0.0	3.2	5.2	0.7	1.4	1.6	0.0
1133	200x230	84.1	0.0	1.2	7.2	0.3	7.2	0.0	0.0

TABLE 7
Moisture and Ash Data for Sieve Fractions

Coal PSOC-	Sieve Fraction	% Moisture	% Ash Dry Basis
1099	40x60	1.3	11.2
1099	200x230	1.6	11.5
1133	200x230	0.8	19.4

Figure 3. SCHEMATIC OF FISHER TGA SYSTEM

sample weight, both accurately and precisely. Samples are held in a quartz bucket which is suspended from one end of the Cahn balance by a nickel hangdown wire. A quartz tube, positioned around the hangdown wire and sample bucket, enables maintenance of controlled atmosphere conditions. A small furnace can be positioned around the quartz tube for temperature control. The furnace is controlled by a Fisher Linear Temperature Programmer, model 370A. A thermocouple is positioned directly beneath the sample bucket for accurate temperature measurement. This TGA system enables one to continuously monitor small weight changes of a sample under conditions of controlled temperature and sample environment. Oxygen uptake on coal was followed with this system as the gain in weight with time of exposure to air.

4.3.2.2 Procedure

A known weight of coal, approximately 150 mg, was placed in a quartz bucket and suspended from one arm of the Cahn balance. The quartz tube was placed over the sample, the furnace was moved into position and the thermocouple was fixed below the sample. N_2^* , at a flow rate of 300 cc/min, was then passed over the sample for 20 min to displace air. This N_2 was purified by passing through heated copper turnings maintained at 500°C to remove oxygen and then through anhydrous calcium sulfate to remove moisture. Next, the sample was heated in a flow of N_2 from ambient to 200°C (at a rate of 20°C/min) to remove moisture from the coal. The sample was maintained at 200°C until constant weight (usually less than 15 min) was attained. Sample temperature was then adjusted to the desired oxidation temperature,

*The N_2 and air used in this work were research grade, prepared by Air Products Co.

and the gas flow was switched from N_2 to air (300 cc/min). The sample was allowed to oxidize until the desired weight gain was achieved. The air flow was then stopped, N_2 flow was resumed, and the oxidized sample was cooled to ambient temperature.

4.3.3 TMA Procedure for Oxidized Samples

Oxidized coal samples were removed from the TGA unit and examined with the 942-TMA dilatometer system within 24 hr. Samples were prepared for dilatometer study according to the procedure outlined in Section 4.1.2. Standard operating conditions called for a $50^\circ\text{C}/\text{min}$ heating rate and a 1g dilatometer load. A total of five dilatometer experiments were conducted at each level of oxidation. Dilation parameters were reported as 95% confidence values determined from the five runs.

4.3.4 Weathering Studies

As part of the oxidation studies, weathering experiments were conducted to look at room temperature oxidation and to investigate the effect of moisture on this oxidation. The coal used in this work was PSOC-1099. Two separate experiments were carried out.

In the first study, a 2 to 3g sample of 200 x 230 mesh coal was placed in a desiccator in dry air. The moisture was removed from this air by covering the bottom 2 in. of the desiccator with anhydrous calcium sulfate. Samples (150 mg) were removed from this desiccator periodically, stored under dry N_2 for 48 hr, and then examined with the 942-TMA unit. A total of five dilatometer runs were conducted on samples at each stage of weathering. To avoid depletion of oxygen, the desiccator was flushed periodically with fresh air.

Concurrent with this, a second study was conducted in moist air. A 2 to 3g sample of 200 x 230 mesh coal was placed in a desiccator in a humid atmosphere. Eighty-eight-percent humidity (at 25°C) was maintained in the desiccator with a $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ saturated salt solution. Samples were removed from the desiccator periodically, stored under dry N_2 for 48 hr, and then examined with the 942-TMA unit. Five dilatometer experiments were conducted on each sample at each stage of weathering.

5. RESULTS AND DISCUSSION

5.1 Effects of TMA Variables on Swelling and Softening Properties

A series of experiments was conducted to determine the effects of dilatometer variables (heating rate, load, and coal particle size) on the swelling and softening parameters defined with the TMA system (Section 4.1.3). The results of this work can be found in Tables 8 and 9. All values in these tables are reported as 95% confidence values obtained from 5 or 6 experimental runs at each set of conditions.

5.1.1 Transition Temperatures

The transition temperatures monitored in this study were the onset of softening temperature (T_S), the dilation or fusion temperature (T_D), and the resolidification temperature (T_R). Details of how these temperatures were determined may be found in the experimental Section (4.1.3).

5.1.1.1 Onset of Softening Temperature (T_S)

The onset of softening temperature showed a marked increase with increasing heating rate. This was true for all particle sizes examined, under all load conditions (Table 8, Figure 4)*. This result was not surprising in light of the results of past studies (2,22). T_S also exhibited a strong inverse dependence with increasing load. Once

*The data presented in Figure 4 exhibited some variation in the degree of uncertainty associated with each reported value. This is a consequence of the method used for determining transition temperatures. The transition defining T_D , for example, is sharp and well defined; thus the corresponding values show little uncertainty. The transition defining T_S , however, is not as sharply defined; and, consequently, the uncertainty associated with these values is greater.

TABLE 8

Effects of Heating Rate, Load and Coal Particle Size on Transition Temperatures

U.S. Standard Sieve Fraction	Heating Rate °C/min	Transition Temperatures, °C								
		Under 5g Load			Under 1g Load			Under No Apparent Load		
		T _s	T _d	T _r	T _s	T _d	T _r	T _s	T _d	T _r
40	50	370 ± 3	433 ± 3	556 ± 7	375 ± 5	432 ± 6	557 ± 3	390 ± 9	425 ± 4	555 ± 4
x	20	347 ± 7	451 ± 4	521 ± 8	359 ± 6	453 ± 6	524 ± 5	370 ± 5	467 ± 4	527 ± 6
60	3	324 ± 10	434 ± 3	NR*	342 ± 9	428 ± 2	475 ± 2	362 ± 11	432 ± 3	478 ± 4
100	50	377 ± 3	468 ± 1	554 ± 4	385 ± 3	471 ± 1	555 ± 4	413 ± 12	477 ± 8	561 ± 3
x	20	357 ± 3	454 ± 2	524 ± 3	364 ± 6	456 ± 1	525 ± 5	400 ± 12	459 ± 2	526 ± 3
150	3	324 ± 6	437 ± 5	479 ± 6	342 ± 8	434 ± 1	478 ± 5	385 ± 18	436 ± 2	NR
200	50	379 ± 9	462 ± 6	555 ± 9	395 ± 5	468 ± 3	560 ± 4	420 ± 4	467 ± 10	558 ± 5
x	20	374 ± 5	453 ± 3	524 ± 3	379 ± 7	454 ± 1	525 ± 2	403 ± 7	457 ± 1	521 ± 4
230	3	326 ± 6	435 ± 1	NR	335 ± 3	435 ± 1	NR	373 ± 6	437 ± 1	NR
Minus 200	50	389 ± 6	476 ± 1	556 ± 4	412 ± 10	478 ± 3	559 ± 2	426 ± 5	479 ± 3	560 ± 2
	20	380 ± 4	460 ± 1	527 ± 3	391 ± 11	461 ± 2	526 ± 4	418 ± 4	465 ± 1	524 ± 5
	3	368 ± 10	438 ± 2	485 ± 8	379 ± 9	438 ± 1	NR	391 ± 9	441 ± 2	NR

* NR - Not Resolvable Under These Conditions

TABLE 9

Effects of Heating Rate, Load and Coal Particle Size on Volume Changes

U.S. Standard Sieve Fraction	Heating Rate °C/min	Volume Contraction Under Load, %			Volume Expansion Under Load, %		
		5g	1g	NAL	5g	1g	NAL
40	50	9 ± 2	11 ± 2	9 ± 5	97 ± 15	385 ± 29	372 ± 26
x	20	10 ± 5	8 ± 2	11 ± 8	70 ± 12	123 ± 18	149 ± 15
60	3	19 ± 2	16 ± 2	11 ± 9	13 ± 3	56 ± 11	52 ± 15
100	50	28 ± 5	31 ± 5	19 ± 13	312 ± 60	473 ± 27	480 ± 27
x	20	34 ± 1	34 ± 6	25 ± 15	118 ± 11	188 ± 17	251 ± 15
150	3	28 ± 9	37 ± 4	16 ± 8	30 ± 5	62 ± 4	79 ± 19
200	50	47 ± 3	45 ± 4	30 ± 7	644 ± 48	663 ± 27	671 ± 16
x	20	50 ± 3	49 ± 3	25 ± 11	230 ± 17	334 ± 45	394 ± 62
230	3	32 ± 3	29 ± 4	12 ± 8	41 ± 3	77 ± 8	116 ± 7
Minus 200	50	33 ± 2	31 ± 2	ND	302 ± 33	359 ± 39	420 ± 33
	20	35 ± 2	35 ± 2	3 ± 2	109 ± 10	170 ± 8	222 ± 25
	3	35 ± 6	31 ± 6	7 ± 2	31 ± 3	57 ± 9	80 ± 11

NAL - No Apparent Load

ND - Not Detectable

TABLE 9 (Continued)

U.S. Standard Sieve Fraction	Heating Rate °C/min	Total Dilation Under Load, %			Final Contraction Under Load, %		
		5g	1g	NAL	5g	1g	NAL
40	50	105 ± 16	396 ± 32	382 ± 23	165 ± 19	179 ± 17	135 ± 24
x	20	79 ± 15	130 ± 22	160 ± 17	123 ± 13	93 ± 21	55 ± 4
60	3	32 ± 4	72 ± 8	62 ± 9	ND	74 ± 18	26 ± 24
100	50	335 ± 50	504 ± 27	500 ± 40	338 ± 76	170 ± 38	99 ± 46
x	20	152 ± 12	221 ± 13	276 ± 16	162 ± 10	119 ± 29	78 ± 63
150	3	57 ± 9	99 ± 5	91 ± 9	19 ± 25	16 ± 5	ND
200	50	690 ± 40	710 ± 20	700 ± 20	172 ± 93	91 ± 36	62 ± 24
x	20	280 ± 20	380 ± 50	420 ± 70	179 ± 20	138 ± 82	86 ± 73
230	3	73 ± 3	110 ± 10	128 ± 14	ND	ND	ND
Minus 200	50	335 ± 32	390 ± 39	420 ± 33	197 ± 69	125 ± 76	96 ± 17
	20	144 ± 12	205 ± 10	226 ± 28	126 ± 13	92 ± 30	44 ± 36
	3	66 ± 7	88 ± 11	86 ± 13	14 ± 2	ND	ND

Figure 4. EFFECT OF HEATING RATE ON TRANSITION TEMPERATURES (T_s AND T_d) FOR PSOC-337

again, such behavior is well documented in the literature (2,3). A distinct inverse particle size dependence was shown too.

5.1.1.2 Initial Dilation or Fusion Temperature (T_d)

As in the case of the softening temperature, the dilation temperature also showed a noticeable heating rate dependence, although not quite as sharp as for T_s (Figure 4). This behavior was observed under all conditions except for T_d values measured for 40 x 60 mesh coal samples. The discrepancy here arises from the shape of the dilatometer trace. At 50°C/min heating rates, for 40 x 60 mesh coal, the temperature at which dilation began was not well defined. A comparison of a dilatometer trace for 200 x 230 mesh coal and 40 x 60 mesh coal, under the same heating rate (50°C/min) and load conditions, illustrates this point (Figure 5). Such behavior can be rationalized if one considers that T_d corresponds to the temperature at which fusion* of the coal particles becomes sufficient to offer appreciable resistance to the escape of volatile matter (2). It appears that for the 40 x 60 mesh coal, intraparticle swelling occurred prior to complete fusion of the particles. This phenomenon masked the fusion temperature and made assignment of T_d values somewhat arbitrary.

Experiments on 40 x 60 mesh coal at heating rates of 20°C/min also exhibited some intraparticle swelling; however, the fusion temperature under these conditions was more clearly defined. At 3°C/min heating rates no intraparticle swelling was evident and the

*The term fusion as used in this context does not correspond to a cementing together of coal particles per se. Rather, upon carbonization, a plasticizing "fluid" is formed which wets the individual coal particles and disperses the "non-fusible" material so that, in actuality, coal particles no longer exist as such.

Figure 5. COMPARISON OF DILATOMETER TRACES FOR PSOC-337 SIEVE FRACTIONS, 200 x 230 MESH AND 40 x 60 MESH
TMA Operating Conditions: 50°C/min Heating Rate, 1g Dilatometer Load

fusion temperature was sharply defined. These results lend some support to the idea that in order for fusion of coal particles to occur, the plasticizing medium must spread out and wet the surface of the particles (5,28-30). At 50°C/min, for 40 x 60 mesh coal, it appears that wetting of the coal particles does occur rapidly enough, and so intraparticle swelling begins prior to and concurrent with agglomeration. At lower heating rates and for smaller particle sizes, fusion is more complete prior to intraparticle swelling and the fusion temperature is better defined.

Dilation temperatures were essentially independent of load effects over the range of loads studied. In general, no particle size dependence was observed, except for 40 x 60 mesh coal when heated at 50°C/min. A particle size dependency may exist but it is difficult to determine from the data collected in this study due to the problem with 40 x 60 mesh coal.

5.1.1.3 Resolidification Temperature (T_r)

Resolidification temperatures exhibited the same type of heating rate dependence reported for T_d and T_s . Variations in coal particle size and dilatometer load had essentially no effect on T_r .

5.1.2 Volume Changes

The volume changes examined in this study were the initial contraction, the expansion, the final contraction and the total dilation. All of these parameters were defined previously (Section 4.1.3), and the methods for determining them have been discussed.

5.1.2.1 Volume Contraction (V_{IC})

The volume contraction measurements made on PSOC-337 showed little or no load dependence over the range of loading conditions

studied. Examination of Table 9 might lead one to think that a load dependence did exist. However, in the no (apparent) load mode, the dilatometer probe was suspended over the coal sample; and, consequently, these values cannot be taken as a true measurement of contraction.

Heating rates appeared to influence contraction to some extent, but no definite pattern was observed.

The most striking changes occurring in V_{IC} were due to particle size variations. An increase in particle size resulted in a decrease in contraction. Particle size dependence is most likely due to the nature of the fusion process. Evidently, larger particles of coal are more difficult to fuse together than smaller particles. As a result, the fluidity of the larger particles may be lower; and their plastic deformation (contraction) under a load would, therefore, be less. As a further consequence, intraparticle swelling becomes significant and so contraction is not as great.

5.1.2.2 Volume Expansion (V_{EX})

As one might expect, volume expansion exhibited strong heating rate and load dependencies. In all cases V_{EX} increased sharply with increases in heating rate (Figure 6). Variations in volume expansion with load depended on the heating conditions used (Figure 7). For example, at 50°C/min for 200 x 230 mesh coal, variations in V_{EX} with load were slight. At lower heating rates, however, load dependencies were more marked.

Volume expansion was also closely related to particle size. As the particle size decreased, V_{EX} increased. Once again this behavior is probably related to the relative ease of fusibility of the various

Figure 6. EFFECT OF HEATING RATE ON VOLUME EXPANSION FOR PSOC-337

Figure 7. EFFECT OF DILATOMETER LOAD ON VOLUME EXPANSION FOR PSOC-337

size fractions. A more poorly fused coal mass (larger particles) will offer less resistance to the escape of volatile gases and would, therefore, not be expected to swell as greatly.

It should be noted here that upon examination of the dilatometer traces in Figure 5 one observes two maxima for the expansion of 40 x 60 mesh coal. The appearance of this double maxima was not unique for this sample but was found to occur in several cases for various coals (see Figures 8 and 15). This is believed to be due to the nature of the dilation process. Dilation is caused by evolution of volatiles through the plastic coal mass. This phenomenon of volatile evolution and its resultant dilation is not a smooth continuous process as can be seen by the large oscillations shown in Figures 2 and 5. The double maxima observed are believed to be a consequence of this. In most experimental runs two maxima were not observed. In these cases a shoulder was usually observed in the dilatometer trace prior to reaching the dilation maximum (as in Figure 5, trace for 200 x 230 mesh coal). Two possible explanations for the shapes of the dilatometer traces are offered. The appearance of a shoulder or double maximum may reflect two distinct pyrolysis processes which occur over the plastic temperature region. If this is true, and these processes overlap, one would expect to see the double maxima that are observed. An alternative explanation to this is that the large oscillations and double maxima observed for these coals are due to incomplete fusion of the coal particles. That is, the coal particles have fused together sufficiently to lead to dilation but the fusion process is not complete at this stage. Therefore, one might expect inconsistencies or large oscillations while fusion of

coal particles continues. It is not possible to make a decision as to which of these explanations is preferred on the basis of the data presented here.

5.1.2.3 Total Dilation (V_{TD})

In general, the total dilation exhibited the same behavior as volume expansion. This was to be expected since the total dilation was taken as the sum of the expansion and contraction values; and, in almost all cases, the expansion contribution was the dominant term. It was thought that this parameter may be valuable when characterizing swelling phenomena, since it is a measure of the total volume change occurring throughout the plastic region.

5.1.2.4 Final Contraction (V_{FC})

The final contraction was strongly affected by heating rate, load and coal particle size. In many cases, especially under 5g load, the dilatometer behaved as a penetrometer. This was evidenced by the fact that the dilatometer probe was immersed in the semi-coke material after certain runs. In fact, under some conditions the final probe position was below the lowest level attained during the initial contraction. Final contraction transitions were usually sharp, and they rarely extended over a range of more than 5°C in the heating program. From these results, one might infer two points. First, at the temperature of maximum expansion the coal material still maintains a high degree of fluidity. Second, the reactions responsible for producing the gases which cause the coal to swell must end abruptly. Shortly after these reactions cease, the semi-coke solidifies.

5.1.3 Standardization of the TMA Technique

5.1.3.1 Advantages of a Microdilatometer System

The results presented above demonstrate the usefulness of this microdilatometer system for the study of swelling and softening properties of coal. Several parameters are clearly defined with this system which are characteristic of the plastic transitions occurring upon carbonization. This dilatometer system offers several advantages which make it well suited for use as a research tool in the study of plastic properties of coals. First of all, it provides a great deal of flexibility in the choice of heating conditions which can be used. One can operate at any linear heating rate in the range $0.5^{\circ}\text{C}/\text{min}$ to $50^{\circ}\text{C}/\text{min}$, or the system can be used with staged heating programs. This dilatometer is very sensitive, and so the amount of sample needed to make accurate measurements is quite small (~ 20 mg). This small sample size enables one to use rapid heating programs and still maintain uniform heating rates. It is estimated that the heating rates found in typical fixed bed gasification units (Lurgi for example) are of the order of 20 to $50^{\circ}\text{C}/\text{min}$. This system then, should prove useful for modelling coal behavior under these heating conditions.

Temperature transitions for onset of softening and dilation are determined from the derivative of the dilatometer trace (Section 4.1.3). This provides clearly defined transitions and makes assignment of these values much less arbitrary than with some other dilatometer systems. The ability to work at rapid heating conditions provides for more pronounced temperature transitions and volume changes. In addition, under rapid heating conditions the turn-around time from one run to another is greatly reduced when compared to $3^{\circ}\text{C}/\text{min}$ heating programs.

5.1.3.2 Reproducibility of Measurements

The 95% confidence values reported in Table 8 for transition temperatures show that, on the average, reproducibility was quite good. The onset of softening temperatures could be resolved to within $\pm 7^{\circ}\text{C}$. This reproducibility improved if a load was placed on the dilatometer. Under load conditions, T_S was determined to within $\pm 5^{\circ}\text{C}$.

Dilation temperatures could be resolved to within $\pm 3^{\circ}\text{C}$ on average. This is remarkable when one considers the rapid heating rates used in some parts of this study. Resolidification temperatures also showed good reproducibility and were determined to within $\pm 4^{\circ}\text{C}$ on average.

Reproducibilities for volume change measurements varied significantly depending on the experimental conditions. When measured under a load, volume contraction values were generally determined to within $\pm 5\%$ of the original starting volume of the coal. As stated previously, contraction values determined under the no load condition were not a true measure of contraction and will not be discussed further.

On average, volume expansion values were determined to within ± 20 to 25% (based upon the starting volume of coal). This may seem like a wide scatter in expansion values. However, if one considers that, under some conditions used in this study, the volume expansion values were as high as 650% , then a scatter of 25% represents only 4% of the normalized expansion value. Any dilatometer operating conditions which lead to more pronounced volume changes then increase the precision of the volume expansion measurement. Under conditions

which give high expansion values (rapid heating rate, small particle size, and small load), V_{EX} was determined to within ± 4 to 5% (normalized basis). Conditions which led to moderate expansion gave V_{EX} values with a resolution of ± 5 to 10%, and conditions which led to low expansion yielded V_{EX} values with a resolution of ± 10 to 20%.

Total dilation values reflected the same reproducibility found for expansion values. This was due to the fact that the major contribution to the total dilation resulted from the expansion.

Final contraction values have a high degree of uncertainty associated with them. This is probably due to the high fluidity of the coal immediately prior to resolidification and to the rapidity with which resolidification occurs (see Section 5.1.2.4). If resolidification were a slower, more steady process, then the final contraction values would be expected to have a higher degree of reproducibility, as in the case of the other volume transitions measured in this study. The magnitude of the final contraction should provide a qualitative indication of the degree of fluidity attained by a coal prior to semi-coke formation.

5.1.3.3 Standard Operating Conditions

The results of this study have shown the usefulness of this microdilatometer system for the study of swelling and softening parameters of coals. Following this preliminary study, a standard operating procedure was adopted. These standard conditions call for rapid heating (50°C/min), small coal particle size (200 x 230 mesh) and a small load (1g) on the dilatometer probe. Under these conditions, transition temperatures were sharply defined and volume changes were most pronounced. The 1g load may lead to slightly lower

expansion values. However, this slight load is necessary to obtain meaningful contraction measurements, and under 50°C/min heating rates, load had only a slight effect on expansion values. Also, a 1g load offers some stability to the dilatometer probe which provides for a more uniform operating procedure.

5.1.4 Standard Method for Raw Coal Studies

Some concern had been expressed over the possibility of maceral and mineral segregation on grinding and sieving. To minimize these effects, a carefully planned procedure was followed (Section 4.1.1.4). It was necessary to follow this procedure because narrow size fractions were needed for oxidation studies. However, for analysis of raw unoxidized coal samples, there was no need to work with sieve fractions. Therefore, a separate procedure was adopted for the analysis of raw coals. This procedure was identical to that used in the oxidation studies with the exception that the coal used was ground to minus 200 mesh. Grinding the entire coal sample to minus 200 mesh eliminated segregation problems.

A series of experiments was conducted on the minus 200 mesh coal to see the effects of TMA variables on the swelling and softening parameters. Heating rate and load effects observed in this study were essentially the same as those observed for the various sieve fractions. However, T_d values were slightly elevated, and the volume expansion was somewhat lower than one would predict from the results of the particle size studies presented above. This may be an indication that the sample had become slightly oxidized during storage. Work presented in the latter sections of this chapter confirmed these suspicions. Samples were stored under N_2 to reduce this possibility.

However, a minus 200 mesh coal sample contains many very fine particles. These fines might be expected to oxidize rapidly even in atmospheres where the oxygen content is very low (4,41,42). While the samples were stored under N_2 , this gas was not scrubbed completely clean of O_2 . Grinding and sieving procedures were conducted in glove bags in a N_2 atmosphere. These bags were flushed several times with N_2 prior to working with coal samples. While this procedure greatly reduces the O_2 partial pressure in the glove bags, a small O_2 partial pressure would still persist. The samples were stored in this atmosphere for periods as long as two months prior to study in the dilatometer. For these reasons, all further dilatometer work on minus 200 mesh coal samples was conducted within 12 hr of grinding to further reduce the possibility of oxidation.

5.2 TMA Results on Raw Coals

Standard TMA operating conditions (Section 4.2) were employed in the analysis of a range of caking coals. Several coal channel samples and their corresponding lithotypes were examined. The results of this work are summarized in Tables 10 and 11. All values reported in these tables are 95% confidence values obtained from five experimental runs for each sample.

Examination of Tables 10 and 11 illustrates further the utility of this dilatometer system for the analysis of swelling and softening properties of a variety of caking coals. Plastic transition temperatures showed excellent reproducibility over the entire range of coals studied. Volume contraction and expansion measurements also showed good reproducibility. This system was particularly sensitive for volume expansion measurements of high swelling coals ($\pm 4\%$).

TABLE 10
Transition Temperature Data for Raw Coal Samples

Coal PSOC-	Transition Temperatures, °C			
	T_s	T_d	T_e	T_r
1082	411 ± 2	495 ± 4	517 ± 5	NR
1083	408 ± 9	485 ± 4	509 ± 4	528 ± 8
1099	397 ± 4	470 ± 2	546 ± 5	561 ± 3
1100	398 ± 4	470 ± 2	545 ± 2	560 ± 3
1101	404 ± 7	475 ± 5	546 ± 10	556 ± 1
1102	396 ± 5	470 ± 3	542 ± 2	556 ± 4
1103	398 ± 4	470 ± 3	515 ± 6	549 ± 4
1104	392 ± 3	469 ± 4	513 ± 4	550 ± 3
1105	398 ± 7	472 ± 6	521 ± 7	552 ± 5
1106	414 ± 4	487 ± 1	533 ± 8	554 ± 1
1112	428 ± 3	NR	NR	NR
1113	441 ± 2	NR	NR	NR
1114	424 ± 2	507 ± 4	520 ± 2	563 ± 4
1115	428 ± 2	500 ± 2	520 ± 2	572 ± 4
1116	412 ± 6	484 ± 2	522 ± 5	542 ± 5
1117	414 ± 4	483 ± 3	521 ± 11	543 ± 5
1118	417 ± 9	496 ± 3	519 ± 5	533 ± 3
1119	399 ± 4	480 ± 5	518 ± 7	544 ± 7
1133	461 ± 4	521 ± 1	565 ± 3	588 ± 3

TABLE 11
Volume Change Data for Raw Coal Samples

Coal PSOC-	Volume Conversion Factor X_C mils/mg*	Volume Changes, %			
		Initial Contraction	Expansion	Total Dilation	Final Contraction
1082	0.92	30 ± 3	-19 ± 5	11 ± 4	ND
1083	1.03	32 ± 2	53 ± 7	85 ± 7	10 ± 5
1099	0.99	44 ± 5	719 ± 12	765 ± 13	54 ± 30
1100	0.98	45 ± 1	715 ± 10	760 ± 10	108 ± 63
1101	1.01	45 ± 2	695 ± 6	740 ± 5	14 ± 21
1102	0.97	46 ± 2	721 ± 16	767 ± 16	75 ± 42
1103	1.03	45 ± 4	577 ± 50	620 ± 40	313 ± 118
1104	1.07	43 ± 4	588 ± 32	632 ± 36	352 ± 207
1105	1.04	40 ± 3	582 ± 32	622 ± 32	192 ± 117
1106	1.04	40 ± 5	478 ± 56	519 ± 60	163 ± 79
1112	1.02	59 ± 4	ND	ND	ND
1113	1.00	46 ± 4	ND	ND	ND
1114	1.08	48 ± 3	-44 ± 6	5 ± 4	6 ± 2
1115	1.05	47 ± 2	-26 ± 8	21 ± 8	11 ± 4
1116	1.04	36 ± 3	178 ± 38	214 ± 39	13 ± 6
1117	1.07	32 ± 6	159 ± 36	191 ± 38	19 ± 11
1118	0.87	31 ± 2	61 ± 7	93 ± 7	13 ± 7
1119	1.05	40 ± 3	218 ± 45	257 ± 43	66 ± 31
1133	1.11	43 ± 6	503 ± 22	546 ± 26	112 ± 67

* 1 mil = 0.001 inch

Sensitivity decreased with a reduction in swelling, but reproducibility in these cases was still acceptable -- typically within $\pm 10\%$.

The data generated in this study were examined for possible correlations between the plastic parameters and various proximate, ultimate and maceral analyses characteristics (Tables 3 through 5). Figure 8 shows some data on raw coals collected for five coal channel specimens varying in rank from HVB to LV bituminous. The dilatometer traces presented in Figure 8 have been modified slightly for the sake of clarity. That is, the large oscillations shown in Figures 2 and 5 have been removed from these traces to prevent overlap of curves. This figure is presented to demonstrate the wide variations observed in plastic behavior as a function of coal rank. In fact, striking differences in behavior were observed even between coals of the same rank classification. PSOC-1099, PSOC-1103, and PSOC-1116 were all classified as high volatile A bituminous coals as determined by maximum vitrinite reflectance. These three coals exhibited marked differences in transition temperatures and swelling properties. Some of these differences may be explained on the basis of vitrinite reflectance alone. PSOC-1099 had a vitrinite reflectance of 0.89, while PSOC-1103 and PSOC-1116 had reflectances of 0.80 and 0.77 respectively. Clearly PSOC-1099 was of a higher degree of coalification than the other two coals, and this may explain its higher swelling characteristics. The reflectances of PSOC-1103 and PSOC-1116 vary slightly, and on this basis alone one would have expected these two coals to behave in a similar manner. However, they did not. PSOC-1103 contained a relatively high amount of exinite when compared to PSOC-1116. Exinites

Figure 8. RAW DATA FOR FRESH UNOXIDIZED COAL CHANNEL SAMPLES
(Modified for Clarity) Dilatometer Operating Conditions: 50°C/min
Heating Rate, 1g Dilatometer Load, Minus 200 Mesh Coal

are less thermally stable than other macerals; and on heating, they impart to the coal a high degree of fluidity (12). This high fluidity and thermal instability may explain the high swelling nature of PSOC-1103. A high exinite content may also account for the large contraction observed for this coal prior to resolidification. In addition, PSOC-1116 contains 20% more oxygen in the raw coal than PSOC-1103, and this might contribute to its rather low expansion values.

A plot was made of transition temperatures versus coal rank, as determined by vitrinite reflectance (Figure 9). This figure shows that, for the coals studied, all three transition temperatures (T_s , T_d , and T_r) pass through minima. Both the onset of softening and the fusion temperatures exhibited low values in the range of reflectance from 0.76 to 0.90 (R_0 mean-max). Unfortunately no dilatometer work was done for coals of vitrinite reflectance between 0.90 and 1.55, and so the actual minimum temperature values for T_s and T_d may occur somewhere in this region. Resolidification temperatures appear to pass through a minimum at a reflectance of around 0.77. It should be noted that the above statements are only qualitative assessments of the data and that many more samples would have to be examined before a strict statement could be made about the relationships between coal rank and transition temperatures.

Transition temperature data for PSOC-1106, PSOC-1113 and PSOC-1118 have not been plotted in Figure 9. These coals showed anomalous behavior. PSOC-1106 contained an inordinate amount of fusinite and had a vitrinite content less than 50%. The latter two coals both contained disproportionate amounts of oxygen (see Table 4).

Figure 9. DEPENDENCE OF TRANSITION TEMPERATURES ON VITRINITE REFLECTANCE

Shaded Symbols - Raw Coal Channel Samples

Open Symbols - Channel Lithotypes

Additional plots were made to examine the changes in total dilation with vitrinite reflectance (Figure 10), percent carbon content (Figure 11), and percent oxygen content (Figure 12). Figure 10 shows that significant dilation does not occur in coals with vitrinite reflectances less than approximately 0.70. PSOC-1083, which had a reflectance of 0.58, was an exceptional coal. Based upon the behavior of other coals with similar vitrinite reflectances, carbon contents and oxygen contents one would not expect this coal to exhibit swelling tendencies. However, PSOC-1083 showed some dilation (85%). The striking feature about this coal was its very high vitrinite content (93.3%) and very low inert content. Vitrinite is known for its swelling and caking tendencies when of sufficient rank, and thus may be the cause of this swelling behavior.

It appears that for coals with reflectances at or near 0.75 the dilation properties rise sharply to some maximum value. Dilation values should return to zero for coals of vitrinite reflectance at or around 2.05. This value represents the division between LV bituminous coal and semi-anthracite.

The circled points in Figure 10 are data from samples (PSOC-1106 and PSOC-1118) which contained inordinate amounts of inert material (ash plus inertinites). One would expect the corresponding dilation values of these samples to be depressed and this is apparent in Figure 10.

A plot of total dilation versus carbon content (Figure 11) shows no appreciable dilation for most coals with less than 81% carbon content. Above 81% carbon, dilation increased to a maximum (84-85% carbon) and then began to decrease with further increases in carbon

Figure 10. DEPENDENCE OF DILATION ON VITRINITE REFLECTANCE

Figure 11. DEPENDENCE OF DILATION ON CARBON CONTENT OF A COAL

Figure 12. DEPENDENCE OF DILATION ON COAL OXYGEN CONTENT

content. Once again PSOC-1083 showed variations from this general behavior. PSOC-1118 (carbon content 78.9%) also varied from this behavior. This coal varied significantly from the other coals examined in this study, as can be determined by examination of Tables 3 through 5. The high vitrinite reflectance observed for this coal may be responsible for its unexpected swelling behavior.

Figure 12 shows the relationship between the oxygen content found in the raw coals and dilation properties. Since oxygen content closely parallels rank (inversely) in many cases, this figure may simply be a reflection of Figures 10 and 11. For this reason, oxygen content alone probably does not provide a good indication of swelling behavior. However, there appears to be some potential for using oxygen content as a secondary parameter to distinguish between the relative swelling capabilities of two coals of equal rank (Comparison of Tables 4 and 11).

Figure 13 illustrates the strong dependence observed between the total dilation and the width of the temperature region over which dilation occurs ($T_e - T_d$).

5.3 TMA Results on Oxidized Coals

5.3.1 Comments on the Method of Oxidation

Before discussing the results of dilatometer studies on oxidized coals, something should be said about the method used for oxidizing coal samples. As stated in the experimental section, oxygen uptake was monitored as the gain in weight of a coal sample with time of exposure to air. With this method, weight gain at a given temperature and coal particle size could be followed accurately and reproducibly.

Figure 13. RELATION BETWEEN EXTENT OF DILATION AND WIDTH OF THE DILATION TEMPERATURE REGION FOR AS-RECEIVED SAMPLES

However, it should be pointed out that these weight gain measurements are not a true indication of the amount of oxygen which reacted with the coal. In this work, samples were oxidized at temperatures above 70°C. From the discussion of the mechanisms of oxidation (Section 2.4.2), it can be seen that, at temperatures above 70°C, the initial coal-oxygen (peroxidic) complexes formed are unstable and decompose to yield other, more stable, coal-oxygen complexes with the evolution of CO_2 , CO and H_2O . Since carbon and hydrogen are lost from the coal in this process, a simple measure of weight gain on exposure to air will not give a truly quantitative measure of the amount of oxygen reacted with a coal. Rather, this method provides a lower limit for the amount of oxygen added to a coal, and the values for weight gain for a given coal should be compared on a relative basis and not as absolute values.

5.3.2 Oxidation Temperature Study

Given that at oxidation temperatures above 70°C, the initial coal-oxygen complexes formed are unstable and will decompose with the liberation of CO, CO_2 and H_2O , it was decided that the first step in these oxidation studies was to determine what effect the temperature of preoxidation had on altering plastic properties. Samples of 200 x 230 mesh PSOC-1099 were oxidized to a certain weight gain (0.50%) at several temperatures ranging from 75°C to 200°C. The results of this study can be found in Table 12.

Figure 14 presents data for rates of weight gain during pre-oxidation of PSOC-1099 at various temperatures. The rate increases sharply with increasing temperature. For example, as given in

TABLE 12

Effects of Oxidation Temperature upon Plastic Properties of PSOC-1099 (200 x 230 mesh coal)

Weight Gain, %	Oxidation Temp. °C	Oxidation Time, min	Contraction %	Expansion %	Total Dilation, %	T _s °C	T _d °C	T _r °C
0.51	200	1.27	23 ± 1	130 ± 35	153 ± 35	429 ± 5	507 ± 2	547 ± 5
0.53	175	1.57	28 ± 3	247 ± 11	275 ± 12	415 ± 6	499 ± 1	551 ± 3
0.50	150	3.87	35 ± 3	309 ± 22	344 ± 23	402 ± 6	489 ± 4	553 ± 1
0.50	125	15.6	39 ± 3	382 ± 15	420 ± 14	397 ± 7	487 ± 8	557 ± 5
0.50	100	74.0	40 ± 4	402 ± 7	443 ± 4	398 ± 6	491 ± 1	557 ± 8
0.49	75	530.0	42 ± 4	440 ± 25	482 ± 26	394 ± 4	488 ± 1	560 ± 4

Figure 14. WEIGHT GAIN VERSUS TIME FOR AIR OXIDATION OF PSOC-1099 AT SEVERAL TEMPERATURES

Table 12, when the temperature of oxidation was reduced from 200°C to 75°C the time required to reach a weight increase of about 0.5% rose 500-fold.

Table 12 also shows that as the temperature of oxidation rose, the reduction in plastic behavior of the coal became greater. An increase in oxidation temperature brought about reductions in contraction, expansion and total dilation and in the resolidification temperature. At the same time, softening and dilation temperatures increased.

The results provide some evidence that the initial coal-oxygen complexes formed are decreasingly stable as the oxidation temperature increases. At all temperatures, two processes occur concurrently, that is pick up of oxygen on the coal and removal of hydrogen and carbon from the coal as CO, CO₂, and water. The latter process becomes of increasing importance as temperature is increased. Therefore, the weight gains which are shown to be constant with increasing temperature in Table 12, in fact, mean that the amount of oxygen added to the coal increased monotonically with increasing oxidation temperature.

It should also be noted that at higher oxidation temperatures (200°C, 175°C) the weights reported in Table 12 contain an added source of error. Following oxidation, the air flow (oxidizing gas) was switched to N₂ and the sample was cooled to room temperature and weighed. At 200°C and 175°C a detectable amount of weight was lost on cooling; presumably due to the instability of the initial coal-oxygen complexes. Therefore, the final weights recorded for these samples were artificially low.

There was no temperature region looked at in this study where oxidation effects were independent of oxidation temperature. From these results, it was decided to conduct all further oxidation work at the same temperature so that the relative amounts of weight gain could be compared meaningfully. The temperature selected for this work was 125°C since, at this temperature, one could reach the desired levels of weight gain (0 to 3%) in a reasonable amount of time (within 12 hrs.).

5.3.3 Effects of Oxidation on Swelling and Softening Properties of Selected Coals

PSOC-1099, a high volatile A bituminous coal known to have high swelling characteristics, was oxidized to several levels of weight gain; and these oxidized samples were then analyzed with the 942-TMA unit. The results of this study can be found in Table 13.

Figure 15 illustrates the dramatic effects that preoxidation had on the swelling and softening behavior of PSOC-1099. As in the case of Figure 8, the dilatometer traces presented here have been simplified to avoid confusion. In general, additions of small amounts of oxygen brought about substantial reductions in volume expansion and contraction values, increases in softening and dilation temperatures, and a slight decrease in the resolidification temperature.

A more detailed picture of oxidation can be seen in Figure 16. Initially, additions of oxygen (< 0.1% wt. gain) caused an increase in expansion values. This same behavior was observed for another HVA coal (Table 14). Further oxidation brought about a sharp, almost linear, decrease in expansion values until approximately 1.5% weight gain was reached. Above this level, expansion changes become less

TABLE 13

Effect of Oxidation Level at 125°C on Subsequent Behavior of PSOC-1099 upon Heating

Weight Gain %	Contraction %	Expansion %	Total Dilation %	Final Contraction %	T _s °C	T _d °C	T _r °C
Fresh Coal	41 ± 11	703 ± 17	744 ± 18	53 ± 64	393 ± 3	475 ± 2	559 ± 3
*	50 ± 3	755 ± 22	805 ± 24	88 ± 48	395 ± 7	475 ± 2	559 ± 3
0.10	50 ± 2	728 ± 26	777 ± 28	107 ± 51	385 ± 5	473 ± 2	555 ± 2
0.24	45 ± 5	650 ± 8	695 ± 8	85 ± 30	389 ± 2	479 ± 2	555 ± 4
0.33	43 ± 6	552 ± 29	595 ± 27	122 ± 48	390 ± 1	483 ± 3	554 ± 4
0.50	45 ± 3	435 ± 17	479 ± 16	118 ± 67	397 ± 7	487 ± 8	557 ± 5
0.72	44 ± 6	269 ± 15	313 ± 14	55 ± 50	398 ± 3	484 ± 4	550 ± 3
0.75	39 ± 3	229 ± 29	268 ± 29	43 ± 40	397 ± 4	494 ± 1	546 ± 4
0.99	40 ± 4	144 ± 16	183 ± 12	17 ± 10	396 ± 11	491 ± 3	543 ± 4
1.31	37 ± 6	49 ± 8	86 ± 10	ND	411 ± 7	492 ± 3	ND
1.48	38 ± 5	-8 ± 10	30 ± 8	ND	412 ± 7	516 ± 2	ND
1.99	48 ± 4	-48 ± 4	ND	ND	417 ± 5	ND	ND
2.74	30 ± 2	-30 ± 2	ND	ND	418 ± 9	ND	ND

* - Coal Stored 80 Days Under N₂

Figure 15. TMA OXIDATION DATA FOR PSOC-1099 (HVA COAL)
(Modified for Clarity) Dilatometer Operating Conditions:
50°C/min Heating Rate, 1g Dilatometer Load, 200 x 230
Mesh Coal

Figure 16. EFFECT OF LEVEL OF OXIDATION ON VOLUME EXPANSION DURING HEATING OF PSOC-1099

TABLE 14

Effect of Oxidation Level on Volume Expansion for PSOC-1103

Weight Gain %	Expansion %
Fresh Coal	577 ± 50
*	616 ± 39
0.05	650 ± 51
0.10	587 ± 75

* - Coal Stored 119 Days Under N₂

sensitive to oxidation and also dilation essentially no longer occurred. It should be pointed out that above 2% weight gain on oxidation the volume expansion curve appears to increase on further oxidation. This results from the method used to determine volume expansion values. Expansion is calculated as the displacement of the dilatometer probe from the baseline. At 2.0% wt. gain there is no expansion of the sample following the initial contraction and so the displacement from the baseline is a negative value. Above 2% wt. gain contraction values decrease and this gives rise to the apparent increase in expansion. In reality, above 2% wt. gain, there is no expansion of the coal sample.

Oxidation studies were also carried out on a higher rank, LV bituminous coal (PSOC-1133). This coal exhibited high swelling much like PSOC-1099. The dilatometer data can be found in Table 15 and in Figure 17. The initial dilation increase observed for the two HVA coals did not occur in the case of PSOC-1133. Loss of dilation properties began immediately upon oxidation.* This coal was much more sensitive to oxidation than PSOC-1099. That is, all swelling properties were removed with less than 1% weight gain upon exposure to air at 125°C. Dilation temperatures increased sharply with increased oxidation, while softening and resolidification temperatures varied only slightly.

* It should be noted that the smallest oxygen loading for sample PSOC-1133 was 0.10% by weight. The possibility then exists that the swelling of this coal also passes through a maximum at lower levels of oxidation. However, from examination of Figure 16, this does not appear to be a likely possibility.

TABLE 15

Effect of Oxidation Level on Subsequent Behavior of PSOC-1133 Upon Heating

Weight Gain %	Contraction %	Expansion %	Total Dilation %	Final Contraction %	T _s °C	T _d °C	T _r °C
Fresh Coal	41 ± 3	473 ± 29	514 ± 29	75 ± 38	463 ± 2	523 ± 1	586 ± 7
0.10	40 ± 3	343 ± 15	331 ± 17	20 ± 12	455 ± 3	525 ± 2	583 ± 4
0.25	35 ± 4	255 ± 17	292 ± 16	9 ± 7	463 ± 4	531 ± 2	585 ± 3
0.43	36 ± 4	99 ± 31	134 ± 34	ND	462 ± 3	541 ± 3	ND
0.56	32 ± 4	14 ± 8	47 ± 11	ND	466 ± 6	548 ± 2	ND
0.75	35 ± 6	-35 ± 6	ND	ND	463 ± 2	ND	ND
1.00	27 ± 2	-27 ± 2	ND	ND	466 ± 4	ND	ND

Figure 17. EFFECT OF LEVEL OF OXIDATION ON VOLUME EXPANSION DURING HEATING OF PSOC-1133

The difference in dilation behavior between the LV bituminous coal and the two HVA coals at low levels of oxidation is believed to be due to the large difference in fluidity between these samples. Maximum Gieseler fluidities were measured for the fresh coal samples by Mr. Joseph Senftle at The Pennsylvania State University Coal Research Section. These values were measured according to ASTM standards (77) as:

PSOC-1099	14,681 DDPM
PSOC-1103	29,944 DDPM
PSOC-1113	58 DDPM

Weathering studies, also conducted by Mr. Senftle, have shown that the Gieseler fluidity for PSOC-1099 drops off very rapidly during the first two weeks of exposure to air at room temperature. In this time, the maximum Gieseler fluidity was reduced by over 60%. The coal used in this work was minus 60 mesh, and it is estimated that the amount of oxygen chemisorbed in this time frame was certainly less than 0.1% (see weathering study data Section 5.3.4). This decrease in fluidity of the plastic coal mass may be the cause of the observed increase in dilation upon slight oxidation. Lower fluidity increases the resistance to escape of volatile gases. That is, the volatile pyrolysis products will require a longer time to escape from the less fluid (more "viscous") material. The increased residence time of the gases in the plastic mass may well lead to an increase in internal gas pressure and a subsequent increase in swelling. An increase in swelling was not observed for the LV bituminous coal because the fluidity was very low for the original fresh coal. Initial oxidation could not bring about the same large decrease in fluidity observed for PSOC-1099.

The fact that swelling of PSOC-1099 upon heating went through a maximum with increasing extent of oxidation (decreasing maximum fluidity) indicates that factors other than coal fluidity also play a role in determining the extent of swelling. As seen in Figure 18, as the coal was oxidized and fluidity was decreased, the dilation temperature rose steadily. An increase in T_d should result in a decrease in the amount of volatile gases available to produce swelling. That is, as T_d rises a larger percentage of the total pyrolysis gases escape from the coal particles before fusion of the particles is sufficient for swelling to begin. A smaller percentage of total volatile release while the coal particles are in the plastic state then results in a decrease in dilation.

The strong dependence of dilation temperature upon the amount of oxygen added to a coal suggests that the role of oxygen in reducing plastic properties is that it inhibits the fusion of coal particles. Schmidt and coworkers (58,59) have shown that oxidation leads to a reduction in the yield of tars produced on carbonization. Evidently some of these tars make up the plasticizing fraction which is responsible for fusion of the coal particles. The fusion temperature reflects this loss in plasticizing medium and so represents a sensitive measure of the degree of oxidation of a coal.

In order for significant swelling of a coal to take place, the coal particles must first fuse together. In the previous section (5.2) the relation was shown between the amount of swelling observed for a coal and the width of the temperature zone from the fusion point to the point of maximum dilation ($\Delta T = T_e - T_d$). A similar relation was observed for oxidized coals (Figure 19). The

Figure 18. EFFECT OF OXYGEN ADDITION ON DILATION TEMPERATURE FOR PSOC-1099

Figure 19. RELATIONSHIP BETWEEN EXTENT OF DILATION AND WIDTH OF THE DILATION TEMPERATURE REGION FOR PREOXIDIZED COALS

width of this temperature region may be determined by the amount of plasticizing material formed in the coal during heat treatment. Evidence exists (58,59) that, upon oxidation, the amount of this material is reduced and so ΔT would become smaller. This correlation then may be due to a relationship between ΔT and the amount of plasticizer present in a coal. Dilation is not related solely to the fluidity attained by a coal however. It also depends upon the volume of volatile gases given off over the range of ΔT . In the case of oxidation, the amount of volatiles given off over the range of ΔT decreases as ΔT decreases. Thus dilation also decreases.

5.3.4 Results of Weathering Studies

A weathering study was designed to look at room temperature oxidation of coals and to investigate the effect of moisture on the rate of weathering. The coal used in this work was PSOC-1099. Samples of coal were allowed to weather in both dry and moist air for various periods of time. These samples were then studied with the DuPont 942-TMA unit. The results of these studies can be found in Table 16.

As seen, on weathering, the dilation values of PSOC-1099 first rose to a maximum value and then began to decrease. In fact, it was shown here that the weathering process began immediately upon grinding of the coal to 200 x 230 mesh. After storage of the coal for 80 days in N_2 the dilation values increased significantly. It should be noted that while samples were stored under N_2 , this gas was not scrubbed completely clean of O_2 . Prolonged storage of samples in this atmosphere showed definite signs of oxidation.

TABLE 16

Effect of Weathering on Subsequent Behavior of PSOC-1099 Upon Heating

Weathering Time Days	Contraction %	Expansion %	Total Dilation %	T _s °C	T _d °C	T _r °C
Fresh Coal	41 ± 11	703 ± 17	744 ± 18	393 ± 3	475 ± 2	559 ± 3
*	50 ± 3	755 ± 22	805 ± 24	395 ± 7	475 ± 2	559 ± 3
Weathering in Dry Air						
13	47 ± 4	769 ± 15	817 ± 13	387 ± 3	472 ± 1	559 ± 2
25	50 ± 5	754 ± 19	804 ± 24	390 ± 2	477 ± 1	557 ± 2
44	48 ± 4	748 ± 15	796 ± 16	390 ± 4	477 ± 2	556 ± 2
65	50 ± 3	746 ± 41	796 ± 43	396 ± 5	482 ± 4	561 ± 2
94	48 ± 6	709 ± 56	758 ± 60	390 ± 8	479 ± 3	558 ± 1
Weathering in Moist Air						
13	49 ± 3	759 ± 33	808 ± 33	389 ± 4	477 ± 1	557 ± 4
25	48 ± 5	695 ± 38	743 ± 38	392 ± 4	479 ± 4	555 ± 1
44	48 ± 3	673 ± 41	721 ± 40	395 ± 7	480 ± 3	556 ± 2
65	47 ± 4	651 ± 47	697 ± 49	395 ± 7	483 ± 5	560 ± 3
94	47 ± 5	577 ± 26	624 ± 26	397 ± 5	483 ± 2	556 ± 5

* - Coal Stored 80 Days Under N₂

This result points up the great difficulty involved in trying to obtain truly "fresh unoxidized" coal samples. Special precautions were taken in this work to minimize oxidation of the samples prior to use. However, even with these precautions, the samples still showed signs of oxidation. The amount of oxygen required to alter the plastic properties of a coal is indeed small. From these results it is recommended that in the future all storage of samples be done with as large a particle size as possible. Grinding of samples should not be undertaken until immediately prior to working with the coals. If prolonged storage of fine coal particles is necessary, this should be either done under high vacuum conditions or under N_2 or Ar of the lowest O_2 and water contents.

The data in Table 16 show that exposure of coal to dry air had much less effect on subsequent volume expansion of PSOC-1099 upon heating than did exposure to wet air. This suggests that water is interacting with oxygen groups on the coal surface. It is known that oxidation of carbons in the presence of moisture leads to surface peroxide formation (53), and thus this result lends some support to the theories of Jones and Townend (54) and Chakravarty (55) as to the formation of peroxygen groups being an important step in the coal oxidation mechanism. The presence of moisture would speed up the oxidation process in this case. One might expect this kind of surface interaction to bring about an increase in the number of acid hydroxyl groups on the coal surface; and, therefore, these results also lend support to the theory that condensation reactions between acid hydroxyl groups lead to crosslinking and a subsequent loss in plastic properties (67-73).

5.3.5 Particle Size and Grinding Study

Kinetic studies have shown that oxidation is a surface phenomenon (4,41,42) and suggest that low temperature oxidation is controlled by diffusion of oxidation through coal particles. VanKrevelen (12) shows the formation of "oxidation edges" on coal particles, and Sevenster (49) discusses the diffusion limitations of low temperature oxidation. With this in mind, one might expect to find a higher concentration of oxygen groups at the outer edges of coal particles. A study was conducted to test this hypothesis. Several 40 x 60 mesh samples (PSOC-1099) were oxidized to various levels. These samples were split and one half of each sample was ground to pass through a 200 mesh sieve. The oxidized samples, both 40 x 60 mesh and minus 200 mesh, were then tested in the dilatometer. The results of this work can be found in Table 17. Figure 20 is a plot of expansion values normalized for expansion of the raw unoxidized samples. This figure shows the partial restoration of dilation upon grinding to expose new surface.

This result suggests that one of the roles of oxygen in the reduction of plastic properties is that of preventing the plasticizing medium from wetting and softening the coal particle surfaces. If the plasticizing fluid is prevented from softening the coal particle surfaces then fusion of the particles will not occur. On grinding, new surface is exposed and it is believed that the plasticizing "fluids" have access to these surfaces. Therefore, fusion occurs at a lower temperature and the resulting dilation is higher.

TABLE 17

Effect of Oxidation Level and Grinding on Subsequent Behavior of PSOC-1099 Upon Heating

Weight Gain %	Contraction %	Expansion %	Total Dilation %	T _s °C	T _d °C	T _r °C
Oxidation of 40 x 60 Mesh Coal						
Fresh Coal	7 ± 3	591 ± 20	598 ± 18	386 ± 5	467 ± 1	558 ± 4
0.25	ND	516 ± 33	516 ± 33	389 ± 6	475 ± 2	559 ± 3
0.48	ND	304 ± 34	304 ± 34	399 ± 12	486 ± 3	555 ± 4
0.79	ND	99 ± 12	99 ± 12	417 ± 3	503 ± 4	543 ± 5
1.00	ND	51 ± 11	51 ± 11	414 ± 3	509 ± 3	547 ± 4
Oxidation Followed by Grinding to -200 Mesh						
Fresh Coal	44 ± 3	742 ± 13	785 ± 13	399 ± 2	471 ± 2	558 ± 1
0.25	49 ± 8	692 ± 42	740 ± 50	393 ± 7	476 ± 1	558 ± 2
0.50	36 ± 5	439 ± 50	474 ± 51	395 ± 6	479 ± 2	552 ± 6
0.78	32 ± 3	199 ± 26	232 ± 24	411 ± 7	493 ± 1	554 ± 3
0.99	35 ± 2	108 ± 15	142 ± 15	408 ± 6	493 ± 3	543 ± 4

Figure 20. EFFECT OF GRINDING PREOXIDIZED SAMPLES ON RESTORING PLASTIC PROPERTIES OF PSOC-1099

6. CONCLUSIONS

This study was an attempt to: a) establish a satisfactory method of quantifying the swelling and softening properties of selected caking coals and b) to use this method to monitor the changes in these properties upon mild oxidation of coals. The ultimate goal was to gain a better understanding of the coking mechanism, in general, and of the subsequent effects of oxidation on this mechanism, in particular. This type of information is essential if one wishes to fully utilize the vast reserves of caking coals found in this country.

The results of this investigation have shown the utility of a microdilatometer system as a research tool for the study of swelling and softening properties of a variety of caking coals. Several parameters are clearly defined by this system which are characteristic of the plastic transitions occurring upon carbonization. On average, reproducibility in the measurement of these parameters is quite good. This system is particularly sensitive for high swelling coals. Sensitivity decreases with a reduction in swelling, but reproducibility in these cases is still acceptable.

This microdilatometer unit provides several features which make it a valuable research tool well suited to studies of this type. First of all, it offers a great deal of flexibility in the choice of heating conditions. The dilatometer is very sensitive, and so the amount of sample needed to make accurate measurements is quite small. This small sample size enables one to use rapid heating programs (50°C/min) and still maintain uniform heating rates. This heating rate capability should prove useful for modelling coal behavior under

heating conditions observed in typical fixed bed gasification units (Lurgi for example). The turn-around time from one run to another (when operating under rapid heating conditions) 20-50°C/min is greatly reduced when compared to 3°C/min heating programs. This ability to work at rapid heating conditions provides for more pronounced temperature and volume transitions. Also, the derivative circuit incorporated in this system provides clearly defined transition temperatures for the onset of softening and initial dilation of a coal sample.

The dilation parameters measured with this unit are influenced significantly by coal particle size, dilatometer load, and heating rate. All transition temperatures measured are strongly dependent on heating rate. Softening temperatures exhibit a distinct decrease with increasing load and particle size. Dilation temperatures are essentially independent of load effects under the conditions of this study. The influence of particle size on T_d cannot be stated for certain. Resolidification temperatures are independent of dilatometer load and coal particle size.

Volume contraction measurements show little or no load dependence under the conditions employed in this study. The most striking changes occurring in V_{IC} are due to particle size effects. V_{IC} increases with decreasing particle size. Volume expansion exhibits strong heating rate and load dependencies. In addition, V_{EX} is closely related to particle size. It appears that larger coal particles do not fuse together as readily as smaller particles. Final contraction measurements exhibit a high degree of uncertainty. This suggests that immediately prior to resolidification the coal still maintains a significant fluidity and that reactions leading to resolidification occur rapidly, over a narrow temperature range.

A wide variation in plastic behavior is observed as a function of coal rank. The onset of softening, initial dilation, and resolidification temperatures appears to pass through minima in the range of caking coals. Values of total dilation pass through a maximum for coals of vitrinite reflectance in the range from 0.90 to 1.55 or carbon contents in the range 83.5% to 87% carbon (daf). Coals with high amounts of exinite, inertinite, ash or oxygen behave differently from most coals of equal rank.

Small increases in the weight of coal during preoxidation (1 to 2%) bring about drastic changes in swelling and softening properties. In general, oxidation brings about substantial reductions in volume expansion and contraction, increases in softening and dilation temperatures, and a slight decrease in resolidification temperatures. For coals which exhibit rather high Gieseler fluidities, slight oxidation may bring about an increase in expansion values prior to destruction of swelling properties.

In order for a coal to swell and form a coke, fusion of coal particles is essential. The strong dependence of fusion temperature (T_d) upon the amount of oxygen added to a coal suggests that the role of oxygen in reducing plastic properties is that it inhibits the fusion of coal particles. This rise in fusion temperature most likely reflects a loss in plasticizing "fluid" and is a sensitive measure of the degree of oxidation of a coal (over a limited range of oxygen uptake).

As the temperature of oxidation rises, for a given level of weight gain, the reduction in plastic behavior of a coal becomes greater. This result is in agreement with the proposed mechanism of

oxidation of coal whereby the initial oxidation step is the formation of coal-oxygen "peroxide" type complexes. These initial complexes become more and more unstable at higher temperatures and decompose to liberate CO, CO₂ and water. Consequently, when measuring oxygen uptake by weight gain, a sample oxidized at higher temperatures shows much more severe oxidation effects.

The results of this study point up the great difficulty involved in obtaining truly fresh "unoxidized" coal samples. Storage of fine coal particles for extended periods of time in atmospheres with even small oxygen concentrations show signs of weathering. It is recommended that, in future investigations, all storage of samples be done with large particle sizes. Grinding of samples should not be undertaken until immediately prior to working with a coal and if prolonged storage is necessary, this should be done under high vacuum or under N₂ or Ar of the lowest O₂ and water contents.

Moisture interacts with oxygen groups on a coal surface and has an enhancing effect on the oxidation process. This behavior lends support to the theory that formation of peroxygen groups on the coal surface is the first step in the oxidation mechanism. This type of interaction would be expected to bring about an increase in the number of acid hydroxyl groups on the coal surface and so this result may lend some support to the theory that condensation reactions between acid hydroxyl groups lead to crosslinking and to a subsequent loss in plasticity.

Plastic properties of an oxidized coal may be partially restored upon grinding to expose new surface.

This microdilatometer unit has been shown to be an excellent system for following the changes in plastic properties of coals upon oxidation. This system is particularly sensitive to changes in expansion values and fusion temperatures. The ability to follow changes in fusion temperature is invaluable since fusion of coal particles is essential for the formation of cakes and cokes. Any treatment which will inhibit this fusion may enable us to utilize these coals more fully. This study shows that fusion can be inhibited by oxidation and by increasing particle size. From the standpoint of the goals of this study, future work should be directed at understanding the fusion process more fully. This should enable us to devise cheaper more efficient methods for eliminating the caking properties which are a source of problems in many utilization schemes.

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