

## Effect of the Chemical and Physical Properties of Carbon Black on its Performance in Polyethylene\*

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### Synopsis

A comprehensive study of the performance of various types of carbon black in polyethylene has been made. The physical and chemical properties of carbon blacks are discussed, and the effectiveness of various blacks as ultraviolet screening agents for polyethylene is assessed. It is seen as a first approximation that primary particle size is the property of the carbon black which largely governs the weatherability of a compound. The data suggest that this is due to that fact that the degree of ultraviolet protection is dependent on the presence of submicroscopic aggregates and their distribution throughout the polymer mass. It is proposed that the aggregate size and distribution are largely controlled by the surface energy arising from the dimensions of the primary particles. Studies of carbon black-antioxidant systems gave results which were in agreement with those of Hawkins et al., who found that carbon blacks having a polar surface exhibit a synergistic behavior with organosulfur type antioxidant, greatly increasing the time required to absorb a given amount of oxygen or undergo thermal degradation. The present study shows that use of antioxidants also contributes to the ability of polyethylene compounds to resist accelerated aging. Outdoor aging of the same compounds are in progress, but more time is required to see if antioxidants are helpful in the manner indicated by the accelerated weathering studies. The effect of carbon blacks on the mechanical properties of polyethylene is discussed, and data are presented to show that higher loadings of carbon black than normally used for ultraviolet protection greatly increase the tensile yield (stress at draw point) at relatively fast rates of applied stress. It is suggested that the use of moderately high concentrations of carbon black would enhance the performance of polyethylene in applications such as pipe which often fails under rapidly applied stress.

### INTRODUCTION

Several million pounds of carbon black are pigmented into polyethylene each year, principally because it has the ability to absorb ultraviolet radiation thus prolonging the life of this type of polymer when used in outdoor applications.

In view of the comparatively fast rate of degradation of the clear polyethylene and the need for long service life on such applications as cable jackets, it is to be expected that the literature abounds in many articles treating the evaluation of carbon black-polyethylene "compounds."

\* Based on paper presented at the 15th International Plastics Congress and Elastomers Symposium, Turin, Italy, September 26-28, 1963.

Indeed the problems of dispersion, dispersion evaluation, degree of protection, extrusion, and the use of antioxidants in combination with carbon blacks have been quite thoroughly investigated by many authors. In these instances most of the emphasis has been placed on the properties of the compounds, except in studies of antioxidants where the role of surface chemistry of the carbon has been stressed.

It is the purpose of the present study to survey generally the performance of various carbon blacks in polyethylene and to attempt to relate the results in terms of the physical and chemical properties of the various grades of the pigment. The significance of carbon black variables such as particle size, degree of structure or aggregation, chemical characteristics of the surface, and changes in the concentration of carbon black has been determined as regards to their effect upon the accelerated and natural aging characteristics and the mechanical properties of polyethylene compounds.

## PROCEDURE

### Preparation of Carbon Black Dispersions

To obtain the maximum value from fine pigments used at low concentrations in practically any system, it is necessary that they be properly dispersed. The polyethylene industry has been especially particular regarding the dispersion of carbon black since so many publications have demonstrated the importance of good dispersion for those applications requiring maximum protection against degradation from ultraviolet radiation.

The many procedures used in the industry for dispersing carbon blacks in polyethylene depend primarily upon the type of equipment available and the degree of dispersion required in the final compound. In the present studies, good dispersions were prepared by procedures accepted by the dispersion industry although not necessarily identical to any specific commercial process.

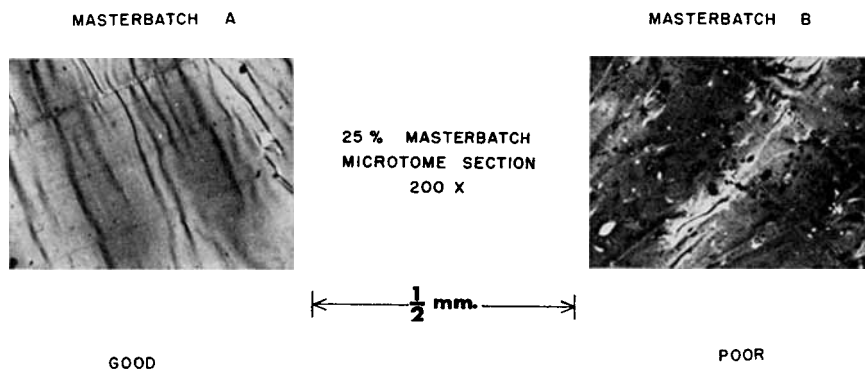
The principle we have followed is to develop high shear in the compound during mixing by using high concentrations of carbon (usually 25%) and a controlled temperature. The exact concentration and temperature depend upon the type of black being dispersed and the particular resin being used. Low density polyethylene (0.923 g./cc.) with melt index of 2.2 was used for studies of weatherability and the relationship of carbon blacks and antioxidants. Another low density polyethylene with melt index of 2.0 has been used for studies of mechanical properties. We have achieved good dispersions by incrementally incorporating the black into the fluxed resin at temperatures sufficiently high to allow good wetting. This step is most conveniently carried out in a Banbury under conditions which minimize compaction of the dry carbon black. The incorporation step is followed by milling at temperatures usually lower than that developed in the incorporation step, such that maximum shear can be developed.

Reductions of the masterbatches to lower concentrations have been carried out successfully either by milling the premixed shredded masterbatch and unpigmented resin or by fluxing the required portion of masterbatch followed by incremental addition of the resin. The latter procedure, although not convenient for certain commercial operations, does parallel accepted procedures used in the reduction of high viscosity dispersions, in that maximum shear is applied at the outset where high shear is desirable.

### Evaluation of Carbon Black Dispersions

Many procedures are available for the evaluation of carbon black-polyethylene dispersions. Although techniques such as electrical methods or opacity measurements have been employed, most methods used by industry involve some form of visual comparison of thin films to designated standard dispersions. The comparison may be entirely subjective for rating dispersions as acceptable or not acceptable, or some counting method may be employed to assign a numerical or alphabetical rating to express the degree of dispersion observed. Most of the films used for observation are prepared by squeezing minute quantities of molten compound between microscope slides (squeeze-outs) and are examined microscopically at magnifications of about  $100\times$  or  $200\times$ .

#### MICROTOME TECHNIQUE



#### SQUEEZE-OUT TECHNIQUE

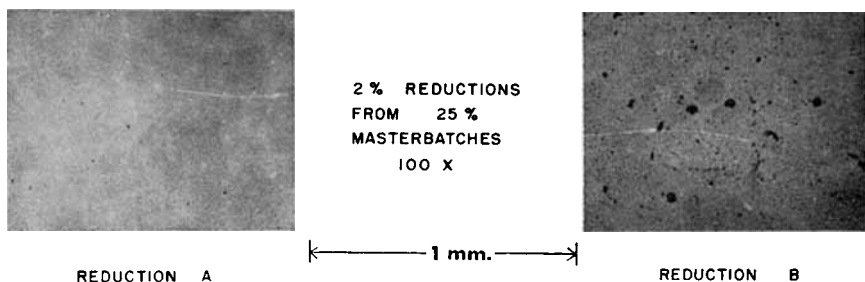


Fig. 1. Evaluation of degree of dispersion.

TABLE I  
Chemical and Physical Properties of Carbon Blacks

Carbon black	Type	Physical Properties				Chemical properties				
		Nigrom- eter index	B.E.T. specific		Diameter $d_m$ A.	Volatiles, %	pH	Total acids, meq./g. <sup>a</sup>	Strong acids (COOH), meq./g. <sup>b</sup>	Weak acids (OH), meq./g. <sup>c</sup>
			surface area, m. <sup>2</sup> /g.	Diameter						
Black pearls 46	Channel	65	800	130	14.0	3.0	2.42	0.46	1.96	
Black pearls 74	Channel	74	332	170	5.0	5.0	0.95	0.06	0.89	
Spheron 9	Channel	85	105	290	5.0	5.0	0.94	0.16	0.78	
Vulcan 9	Oil furnace (SAF)	86	124	200	1.5	8.5	0.84	0.00	0.84	
Vulcan 3	Oil furnace (HAF)	90	74	290	1.0	8.5	0.68	0.02	0.66	
Regal 330	Low structure oil furnace	84.5	—	240	—	8.5	0.42	0.01	0.41	
Sterling S	Gas furnace	99	23	800	1.0	9.5	0.18	0.00	0.18	
Sterling FT	Thermal (FT)	107	13	1800	0.5	8.5	0.12	0.00	0.12	
Sterling MT	Thermal (MT)	110	6	4700	0.5	8.5	0.10	0.00	0.10	

<sup>a</sup> Active hydrogen with LiAlH<sub>4</sub>; procedure as described by Rivin.<sup>3</sup>

<sup>b</sup> Neutralized in NaHCO<sub>3</sub>; procedure as described by Rivin.<sup>3</sup>

<sup>c</sup> Total acids minus strong acids; procedure as described by Rivin.<sup>3</sup>

In preparing dispersions for our studies, we found it advisable to first ascertain the degree of dispersion obtained in the masterbatches before dilution, since this is the most important factor for obtaining satisfactory reductions. The procedure used is the examination of microtome sections prepared according to the method described by Tidmus and Parkinson<sup>1</sup> and later modified by our laboratories for polyethylene dispersions. This direct method allows the examination to be carried out with a minimum of change in the dispersion. Photographs of microtome sections of masterbatches prepared by good and poor procedures (high and low temperature mixing) are shown in Figure 1. Reductions of the masterbatches to 2% concentration were pressed out and similarly compared.

Care was taken in the preparation of the compounds described in the present study to achieve as high a degree of dispersion as possible. All of the compounds were dispersed to an extent equal to or closely approximating the degree achieved in Figure 1A (masterbatch) and 1A (reduction) except where otherwise noted.

Special procedures, such as the determination of the ultraviolet resistance which carbon blacks impart to polyethylene, the method of exposure, and the use of the electron microscope to determine the location of carbon black particles throughout the polymer mass, are described in the discussion.

## RESULTS AND DISCUSSION

### General Properties of Carbon Black

The carbon blacks used in this study range widely in physical and chemical properties. Physically they vary in average particle size, particle size distribution, specific surface area, porosity of surface, and the tendency of the individual primary particles to be associated in chainlike structure. Chemically, they vary in the population and nature of oxygenated structures combined with their surface.<sup>2</sup> Some of these groups display very little chemical activity, but others act as weak or strong acids. Essentially all neutral surface structures are either quinones or acid derivatives (lactones, esters, etc.).<sup>3</sup> Acidic groups can be attributed to carboxylic and hydroxylic acid structures.<sup>3</sup> Channel blacks, which have a relatively high concentration of these polar groups, have an acidic surface. Furnace carbons have fewer polar groups, and these largely consist of the weaker hydroxylic acid structures. The population and nature of these groups varies considerably over the broad spectrum of commercial carbon blacks as evidenced by the pH determinations of aqueous carbon black slurries which encompass values of about 3.0-8.5. The basic pH is due to the aromatic character of the bare or nearly bare carbon surface which is capable of  $\pi$ -complexing protons to form its conjugate acid.<sup>4</sup> Although furnace carbons contain relatively few polar groups, their number is sufficient to bring their pH well below the value of 10 reported<sup>3</sup> for a carbon severely heat-treated to remove all traces of chemisorbed matter.

Table I summarizes the important physical and chemical properties of the carbon blacks used in this study.

As can be readily appreciated from the data presented in Table I, the performance of carbon blacks in practical applications varies greatly from grade to grade. The particle dimensions contribute greatly to reinforcement in rubber or properties in paint and ink vehicles. Yet the degree of reinforcement cannot be solely attributed to dimensions, for the nature of the carbon black surface seems to be involved. Dannenberg<sup>5</sup> points out that the presence of hydrogen atoms bound to aromatic surface carbons or, more likely, carbon atoms located at edges of the graphitic platelets of which the particles are comprised may be responsible for surface activity that could cause rubber-carbon black interaction. Polar groups attached to the carbon surface cause a retardation in the rate of vulcanization but may not significantly contribute to reinforcement in natural SBR, or oil-extended SBR.

On the other hand, the dynamic properties of butyl rubber are greatly improved by the presence of polar groups on the surface of the carbon black particles.<sup>6</sup> Similarly, there is evidence that the performance of carbon blacks in protective and decorative coatings is dependent on the dimensions of particles and on the interaction of the surface with the active vehicles used in these applications.

By comparison to the above elastomers or coating vehicles, polyethylene is quite stable; but because of this virtue, the criterion of its performance is very stringent, and many of the products made from this type of polymer must survive very severe environmental conditions. Cable jackets must last for 20 yr. in outdoor service;<sup>7</sup> extremely thin films for use in agricultural applications must withstand sunlight and the elements for a season or more.

Under these conditions, the stability of the polymer is challenged. The presence of branched chain structures, unsaturated bonds, traces of C=O bonds, and the effect of temperature and milling in the presence of air and subsequent exposure to ultraviolet contribute to an earlier failure than would be expected on the basis of the pure, completely saturated polymer.

Thus chemical reactions may occur and, therefore, the performance of a carbon black in polyethylene must be assessed not only in terms of the physical properties but also in terms of its surface chemistry.

### Weatherability of Polyethylene Compounds

Polyethylene absorbs electromagnetic energy over the range of 250-330 m $\mu$  wavelength.<sup>8</sup> Absorption is generally attributed to impurities in the polymer, particularly those containing C=O bonds. The presence of carbonyl groups may arise from the initial synthesis, processing or fabrication, and oxidation of unsaturated centers at normal temperatures.

Haywood<sup>9</sup> points out that the ultraviolet component of sunlight extends down to a limit of 295 m $\mu$  in the summer, receding to a limit of 310 m $\mu$

during winter, at which time there is a decrease in intensity. The range of wavelength which is of importance in studies of outdoor exposure lies mainly in the range 295–330  $m\mu$ . Over this range the shorter wavelength components actually bring about most of the degradation.

It is important to define as accurately as possible the range of the ultraviolet spectrum which is responsible for degradation, since small particles scatter and absorb electromagnetic energy to an extent that is dependent on the particular wavelength and the diameter of the particle under consideration.

Calculations by Ambrose<sup>7,10</sup> show that maximum attenuation for monochromatic radiation over the range of 200–700  $m\mu$  is dependent on an optimum particle size. The maxima vary in accordance with the wavelength, and the optimum size of the carbon black particles increases as the wavelength increases. Over the range of principle interest (295–330  $m\mu$ ), which for simplicity can be approximated by the attenuation of energy defined by 300  $m\mu$ , the calculations by Ambrose show that the optimum particle size for maximum absorption and scattering is about 100  $m\mu$  diameter. The maximum is quite broad, however, and at 300  $m\mu$  incident light, particles ranging in diameter from 50 to 180  $m\mu$  are as effective as the particles of any size in the attenuation of 350  $m\mu$  wavelength incident light. In the latter case, the optimum is near 120  $m\mu$  diameter.

Cocks and Metzger,<sup>8</sup> in discussing photodegradation of polyethylene, also cite the calculations of Ambrose, to emphasize that carbon blacks which are of 35  $m\mu$  radius (70  $m\mu$  diameter) are most effective in attenuating the ultraviolet radiation which is most active in causing photodegradation in polyethylene.

These values for optimum particle size, whether 70 or 100  $m\mu$ , are an approximate order of 5–10 greater than the average particle size of carbon blacks known to be the most effective ultraviolet screening agents for polyethylene. The present study, for example, clearly shows that blacks having an average primary particle diameter of 10–20  $m\mu$  are among the most effective; and the indications are that the 13  $m\mu$  (ave.) particle is superior to the 20  $m\mu$  (ave.) particle.

This does not suggest that the calculated values are in error but rather indicates that the primary particles of carbon black when dispersed into polyethylene may be associated to form small agglomerates or kinetic units of larger dimensions than those of the primary particles.

Maximum protection from damaging ultraviolet radiation might be expected when these agglomerates approach the dimensions described above and are evenly distributed or dispersed throughout the continuous phase or polymer.

The speculation is advanced that the surface energy due to the dimensions of the primary carbon black particles exerts a strong influence on the size of the aggregates, and for a given energy input during the dispersion, the aggregate size is a function of the primary particle size or surface area.

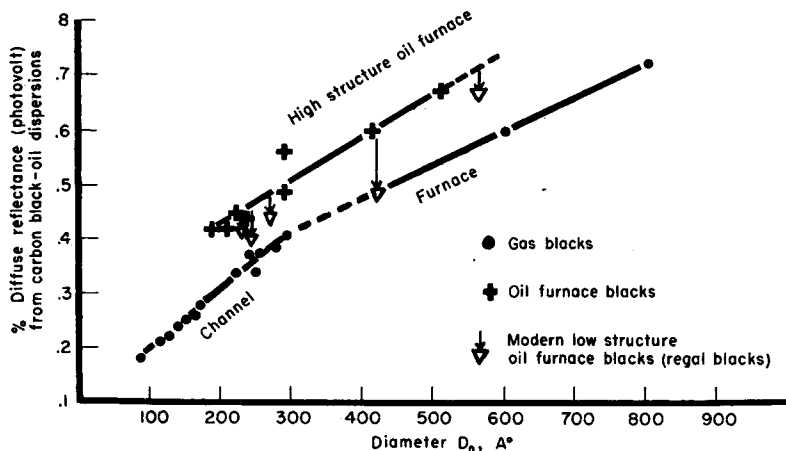


Fig. 2. Per cent diffuse reflectance vs. particle size.

The aggregates or units are encountered whenever carbon is in the dispersed state, and their size varies in accordance with the method of incorporation, the nature of the carbon black, and properties of the continuous phase.

Generally the units comprised of very small particle blacks are smaller than those comprised of large particle size blacks, but the latter aggregates contain fewer primary particles. Voët,<sup>11</sup> in discussing light scattering from carbon blacks dispersed in mineral oil, points out that the units of fine particle size blacks consists of hundreds of elementary particles, while the units of a large diameter black such as an SRF grade consist of relatively few primary particles.

Voët shows an excellent relationship between the specific surface area, using a wide range of carbon blacks and absorbance of 284  $m\mu$  ultraviolet.

Figure 2 shows that per cent diffuse reflectance of white light from the surface of carbon black-oil systems also relates to primary particle size.

It was first necessary, however, to classify carbon blacks of similar nature into two groups: one group consists of carbon blacks and channel and furnace blacks, which have a relatively low degree of "structure;" the other consists of oil furnace blacks, which have a greater degree of "structure." The relationship of a few modern carbon blacks, the Regals, is also presented in this figure. The latter are classified as low structure blacks. The significance of the term "structure" and other differences between the classes of blacks will be discussed later.

For the present it is of interest to note not only the general effect of average particle size, but also the very tangible fact that channel blacks or low structure blacks in general reflect much less light than the relatively high structure furnace blacks of the same average particle size.

This is also evident from Table I where nigrometer scale, a value dependent on diffuse reflectance, is observed to be much higher for the oil



furnace black than for channel blacks of the same average particle size. Both the general relationship and discrepancies above also appear in nearly identical manner when the degree of protection from ultraviolet degradation imparted by various blacks to polyethylene is related to average particle size.

To illustrate the general nature of the relationship, Sterling FT, Vulcan 3, Spheron 9, Vulcan 9, Black Pearls 74, and Black Pearls 46 were dispersed into polyethylene and reduced to 2% concentration. Specimens of 65 mil thickness were exposed for 2200 hr. in the Atlas Weather-Ometer (Model X-W-R without Corax D filters; air temperature 100°F., 50% R.H., water spray 18 min. in 2 hr. cycle).

The criterion of performance used in this study is the degree of surface cracking observed microscopically at 100× after exposure for a designated period of time. The procedure is similar to that used by Gottfried and Dutzer,<sup>12</sup> who investigated the efficiency of organic ultraviolet absorber as protectorants for linear polyethylene. These authors related surface cracking to more conventional indications of failure such as decrease in elongation, melt index, and tensile strength. The optical procedure was used here because it is nondestructive of the specimen, permits differences in performance to be established very quickly, and provides a continuous record of the progress towards failure over the duration of the exposure.

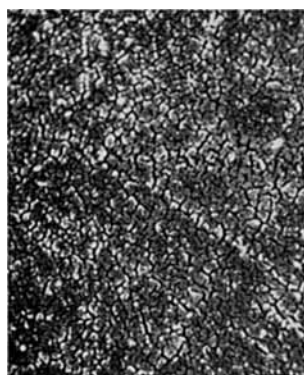
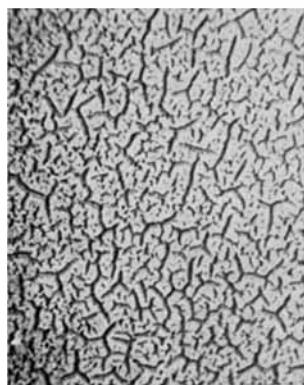
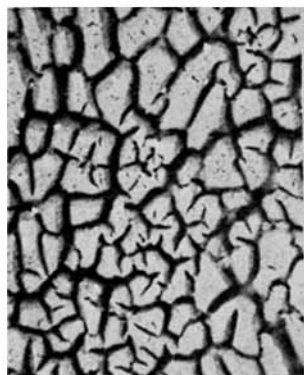
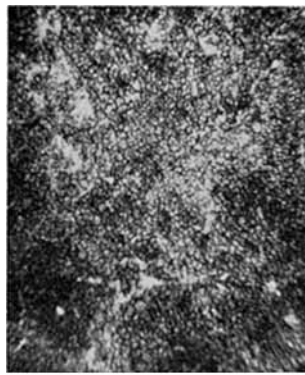
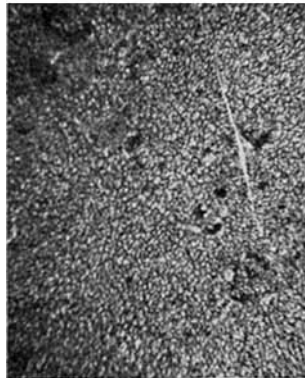
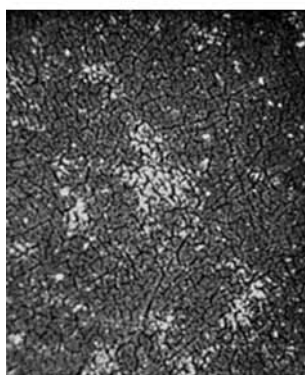
The results of this comparison are shown in Figure 3. In a qualitative way it is observed that the degree of protection increases as the primary particle size of the blacks decrease. Figure 4 shows the effect of aging the same compounds outdoors for 5 yr. at 45° southern exposure at Hanover, Massachusetts. Only those blacks of large particle diameter show failure.

A similar comparison is presented in Figure 5. This time to exaggerate conditions, compounds containing 0.5% black were exposed outdoors for 5 yr. The agreement between the natural and simulated weathering results is quite striking.

Although there is a strong general relationship of average primary particle size to the degree of ultraviolet protection imparted to polyethylene by carbon black, two notable exceptions may be observed in Figures 3 and 5.

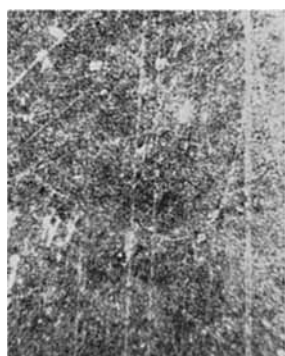
Black Pearls 74, a channel black, is superior to Vulcan 9, a furnace black, each of about 20 m $\mu$  average primary particle size; and Spheron 9 (channel black) is superior to Vulcan 3 (furnace black), each about 30 m $\mu$  average primary particle size. Acheson,<sup>14</sup> has previously reported this phenomenon. This behavior is remarkably similar to that of per cent diffuse reflectance from oil carbon black dispersions and may result from a common factor.

A likely explanation is the deficiency of an average particle size as a means to characterize the physical dimensions of powders having various modes of size distribution. Channel blacks have a relatively narrow and normal distribution, while furnace blacks tend to have a broad distribution which is often skewed.

**VULCAN 9****VULCAN 3****STERLING FT****BLACK PEARLS 46****BLACK PEARLS 74****SPHERON 9**

↕ 1 mm. ↔

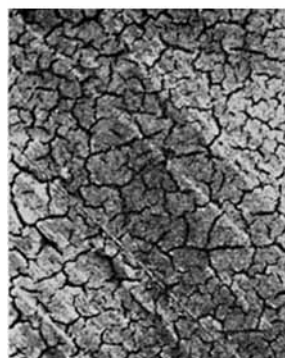
Fig. 3. Accelerated aging of polyethylene compounds; 2% carbon black; 2200 hr. in Weather-Ometer.



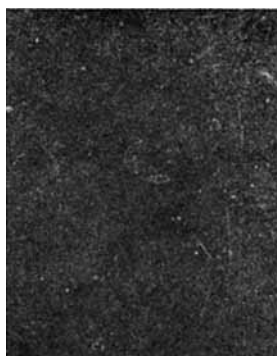
**VULCAN 9**



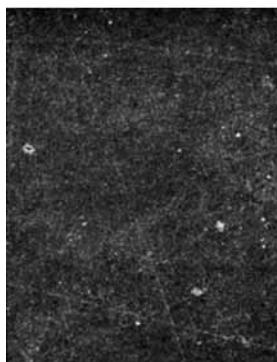
**VULCAN 3**



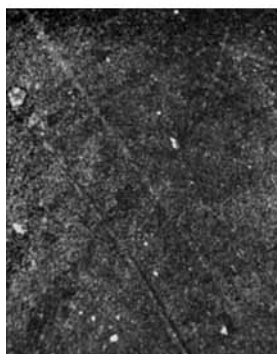
**STERLING FT**



**BLACK PEARLS 46**



**BLACK PEARLS 74**



**SPHERON 9**

1 mm.

Fig. 4. Natural aging of polyethylene compounds; 2% carbon black; 5 yr. at Hanover, Mass.

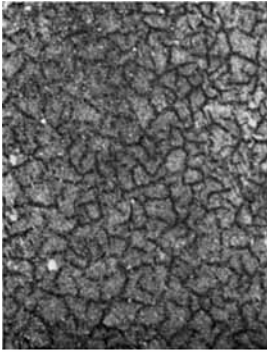
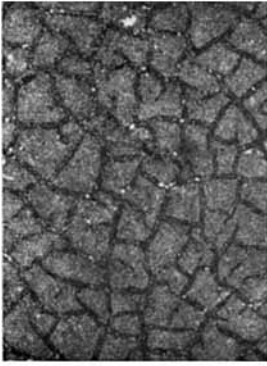
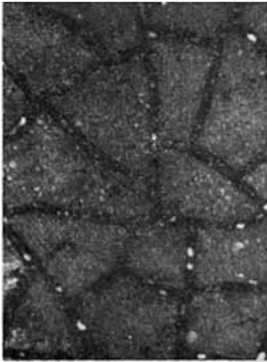
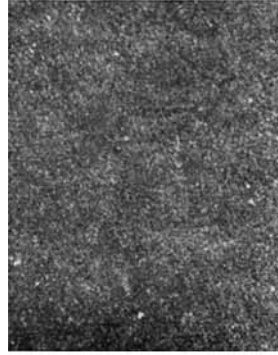
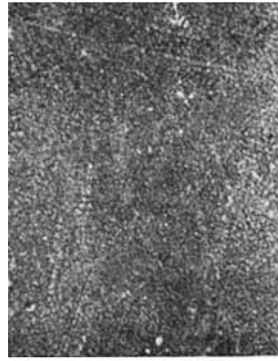
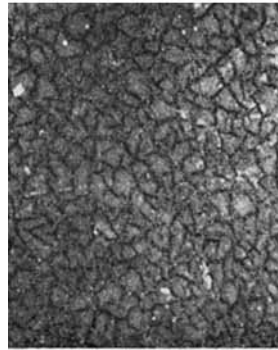
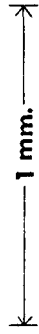
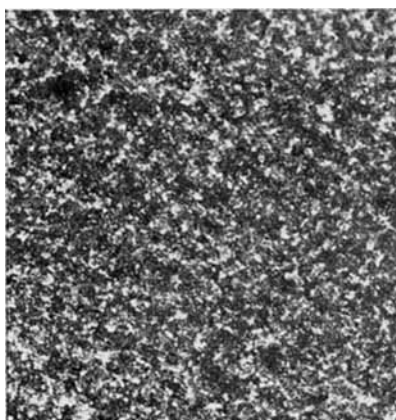
**VULCAN 9****VULCAN 3****STERLING FT****BLACK PEARLS 46****BLACK PEARLS 74****SPHERON 9**

Fig. 5. Natural aging of polyethylene compounds; 0.5% carbon black; 5 yr. of Hanover, Mass.

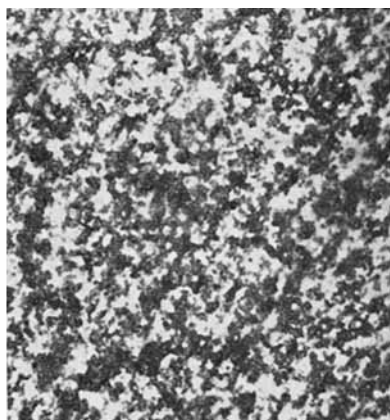
For a given weight of the two types of blacks of the same average particle diameter, the furnace black with its broader distribution has a relatively large number fraction of coarse particles compared to the channel black. The significance of this is that a polyethylene compound at a given weight per cent concentration made from a furnace black actually contains fewer particles per unit volume than that made from a channel black of the same average diameter and, accordingly, a much lesser number of particles to give protection.

Another factor which may also effect the degree of protection from ultraviolet energy is the arrangement of the primary particles and aggregates.

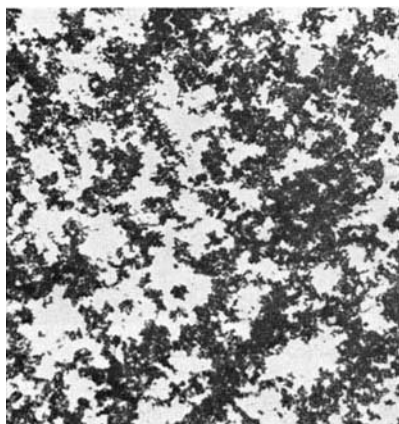
Electron microscopy offers a means to examine such arrangements in the polymer mass. Difficulty is encountered, however, in that ultrathin sections desirable for this type of study are extremely difficult to prepare. The procedure which we used to circumvent this difficulty results in thin



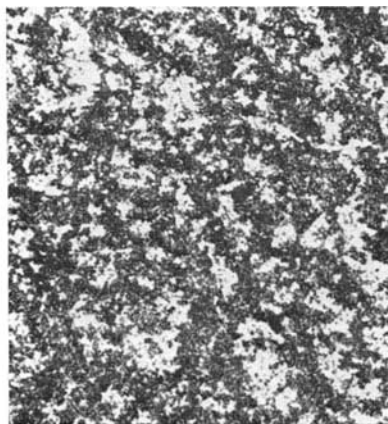
**Black Pearls 74**



**Spheron 9**



**Vulcan 3**



**Regal 330**

Fig. 6. Electron micrographs of 2% polyethylene compounds. Ca. 6950 $\times$ .

films which we believe shows the location of the particles as they exist in the compound. The procedure is discussed here, because it should be made clear that there is a possibility that this technique may alter the location of the particles. Briefly, a specimen of  $1\ \mu$  thickness is obtained by means of a microtome. This is spread carefully on a carbon grid, the spreading facilitated by the use of cold xylene. The specimen is then bombarded by a high intensity beam to remove all but an extremely thin layer of the polymer (dispersion).

Although this is rather rigorous treatment, similar techniques have been employed successfully; for example, Moscou,<sup>14</sup> in studying the dispersion of carbon black in rubber, used cathodic oxygen etching starting with relatively thick sections. He concludes that the particle arrangement was not substantially altered. Nitrogen etching and other means are often used to obtain ultrathin films for electron microscopy.

In our preparations, the electron bombardment of the sample may be considered an etching process. With these reservations, electron micrographs show the particle arrangement of carbon blacks when well dispersed in polyethylene. In Figure 6 electron micrographs show the arrangement of particles of Black Pearls 74, Vulcan 3, Spheron 9, and Regal 330, well dispersed into polyethylene at a concentration of 2.0 wt.-%. The electron micrographs show how the degree of "filling" is dependent on the number of particles. Black Pearls 74 and Spheron 9 are both channel blacks, have relatively low structure, and have relatively narrow particle size distributions. Black Pearls 74, being of smaller particle size than Spheron 9, offers more particles per unit volume at a given weight concentration to more completely fill the polymer.

Vulcan 3 is a structure black and accordingly its particles tend to be associated in aggregates. It has a broad particle size distribution compared to that of Spheron 9, and although the average primary particle size of the two is approximately the same, the Vulcan 3 has fewer particles. This combination of effects is responsible for the relatively larger areas of

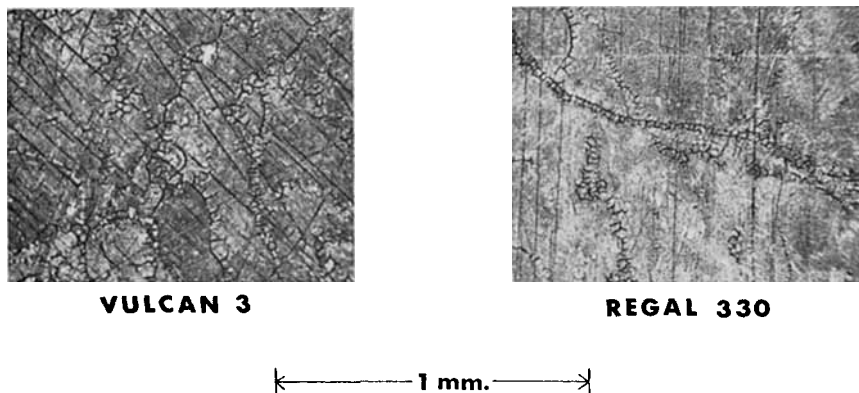


Fig. 7. Accelerated aging of polyethylene compounds; 2.0% carbon black; 1000 hr. in Weather-Ometer.

unprotected polyethylene when Vulcan 3 is used at the same concentration (2%) as Spheron 9 and accounts for the latter's superior protective ability.

Regal 330 is typical of a new class of furnace blacks made by the flame additive process. In this process, additives are injected into the combustion zone, thus modifying the combustion reactions and the properties of the resulting furnace blacks. Such blacks have low oil absorption, perform as low modulus blacks in rubber, and, in general, may be considered to be low structure furnace blacks, approaching the physical properties of channel blacks.

The electron micrograph of the Regal 330 compound is presented to show how a black of reduced structure of about the same average particle size as Vulcan 3 more completely fills the polymer.

Because Regal 330 is a new carbon black, it was not possible to evaluate its ability to protect polyethylene from ultraviolet light in the studies previously described. Therefore, new compounds of Vulcan 3 and Regal 330 were aged in the Weather-Ometer for a preliminary comparison.

Figure 7 shows the progress after 1000 hr. The Regal black is superior at this stage of the evaluation.

Thus the number of particles and their arrangement within the compound, that is the degree and nature of their aggregation, largely governs the degree to which a carbon black protects polyethylene from ultraviolet degradation.

Although the physical properties of carbon blacks largely control their ability to protect polyethylene against the action of ultraviolet light, the chemical properties should also be considered. First there is the possibility that specific groups on the surface of a black may be effective in absorbing ultraviolet. C=O groups, for example, are present on most polar blacks; and these groups may contribute to ultraviolet absorption when associated with particles that are not "screened" by others.

Secondly, as will be discussed next, acidic carbon blacks function as mild antioxidants, presumably accepting polymer radicals, thus terminating chain reactions which lead to thermal degradation. Since the mechanism of thermal degradation should not differ appreciably from that of photodegradation,<sup>9</sup> the surface characteristics may contribute somewhat to the ability of carbon black to impart protection to polyethylene. Furnace blacks which have been subjected to various modes of aftertreatment to add polar groups to their surface, however, show only marginal improvement in weatherability. An assessment of all the properties leads to the conclusion that the physical properties overwhelmingly govern the effectiveness of carbon blacks as protectorants of polyethylene from ultraviolet degradation.

Thus far, studies of the performance of carbon blacks have been made by comparisons of various grades at identical concentrations. It is of interest to compare a few of the carbon blacks over a range of concentrations to first determine the effect of concentration for a given carbon black and secondly to determine the concentration levels necessary to achieve the

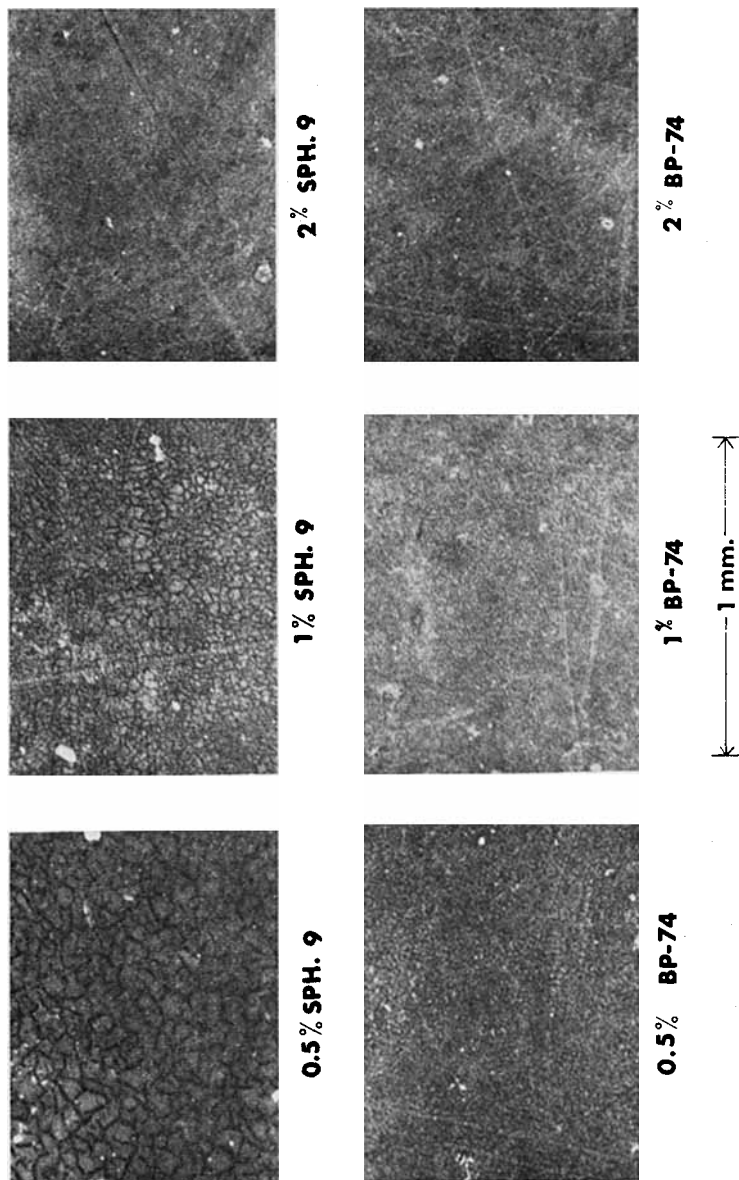


Fig. 8. Natural aging of polyethylene compounds; Spheron 9 vs. Black Pearls 74; 5 yr. at Hanover, Mass.



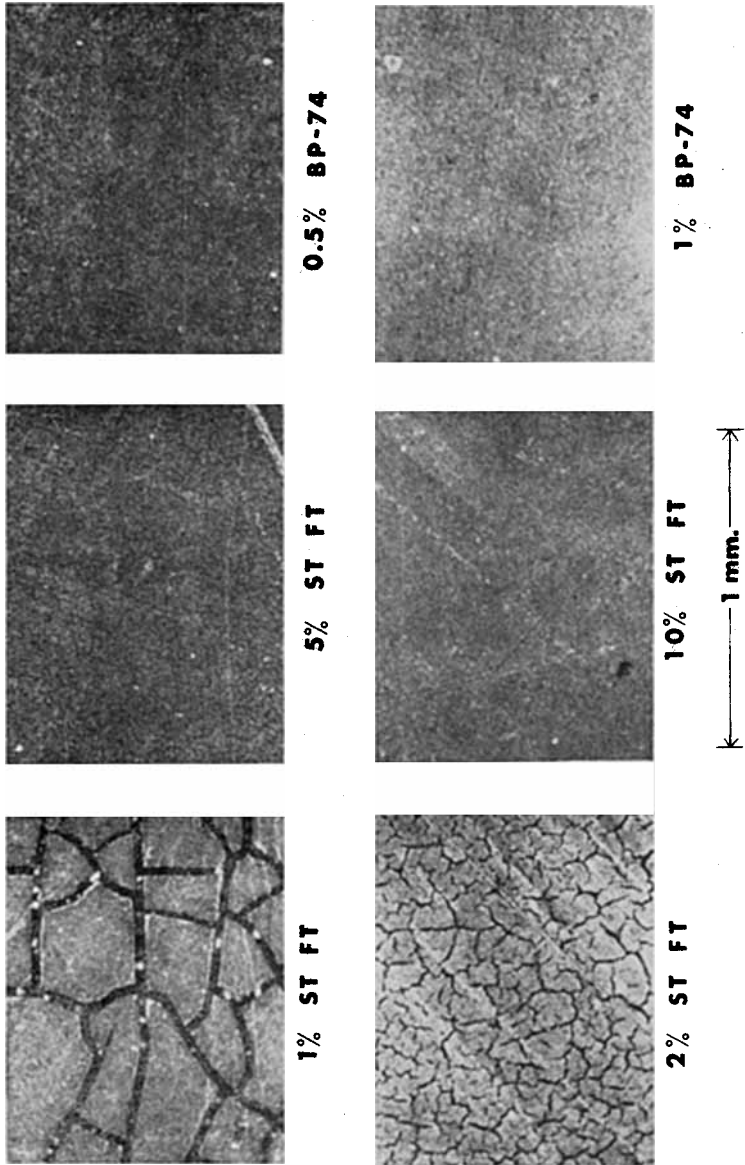


Fig. 9. Natural aging of polyethylene compounds; Sterling FT vs. Black Pearls 74; 5 yr. at Hanover, Mass.

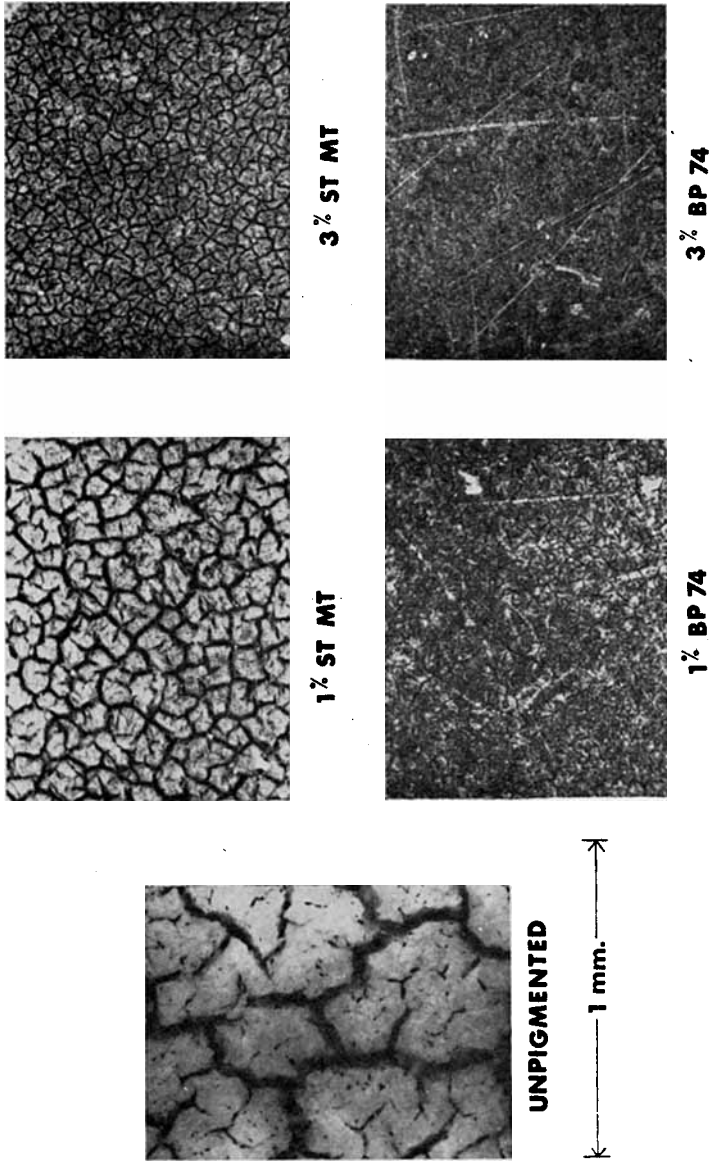


Fig. 10. Natural aging of polypropylene compounds; Sterling MT vs. Black Pearls 74; 5 yr. at Hanover, Mass.

same degree of protection with carbon blacks that vary in dimensions or protective efficiency.

Figure 8 compares the ultraviolet protective ability of Black Pearls 74 and Spheron 9. In this series the compounds contain 0.5, 1.0, and 2% of each black. They were exposed for 5 yr. outdoors at the Hanover location. Concentration of either black is shown to be a predominant factor in the ability of a compound to resist degradation. The comparison further shows that a little over twice as much Spheron 9 as Black Pearls 74 is required to obtain equal performance.

Figure 9 similarly compares Black Pearls 74 to Sterling FT. This is a comparison of one of the smallest particle size carbon blacks available to one of the largest. The effect of concentration is again demonstrated, and in this instance, it is evident that about 5 to 10 times as much Sterling FT as Black Pearls 74 is required to give acceptable protection.

Figure 10 is presented to show that the results are not an individual property of the particular polyolefin chosen for the study. Figure 10 compares Black Pearls 74 to Sterling MT in polypropylene. The results are remarkably similar to those obtained with polyethylene.

Having established the relative concentrations at which Spheron 9 and Sterling FT impart approximately the same degree of protection to polyethylene, it is of interest to calculate the amount of these blacks which would be required to furnish equal protection from the number of particles and their dimensions. Since a particle of diameter  $d$  actually covers an area dependent on  $d$  to the second power, it follows that the product times a constant is a specific surface area. It can be shown that this is the same specific surface area  $S$ , in square meters per gram, usually calculated from electron micrographs of particles.

$$S = 6 \times 10^4 / 1.86d_a$$

where  $d_a$  is the mean surface diameter ( $d_a = \sum nd^3 / \sum nd^2$ ),  $n$  is the number of particles of size  $d$ , and 1.86 g./cc. is the density of the carbon black. The calculations based on diameters,  $d_a$ , are presented in Table II.

The calculated values are in reasonable agreement with the experimental values. The calculated values do not take into account the fact that aggregation occurs. Although no numerical data are available on the aggregate size of the blacks, the aggregates of Black Pearls 74 are smaller than those

TABLE II  
Relative Concentration of Carbon Black to Approximate Ultraviolet Protective Ability of Black Pearls 74

Carbon black	$d_n$ , A.	$d_a$ , A.	$S$ , Calculated	Relative concentration	
				Calculated	Experimental
Black Pearls 74	173	247	131	1	1
Spheron 9	290	345	94	1.4	2-3
Sterling FT	1800	1980	16.3	8.0	5-10

of Spheron 9 (Fig. 6) and, therefore, may lie closer to the optimum size suggested by Ambrose. If the aggregates of Spheron 9, particularly at higher concentrations, are larger than optimum, the differences between the calculated values and experimental results could be reconciled.

In contrast to this, the calculated concentrations for Sterling FT agrees very well with the experimental results. Any degree of aggregation of this black would result in dimensions too large to be near optimum in accordance with the values calculated on the basis of the Mie theory. However, the dimensions of Sterling FT aggregates probably greatly exceed the wavelength of the ultraviolet light. Calculations based on the Mie theory specify that the particles be spherical, that the system be dilute, and that the wavelength of the energy be approximately comparable. It seems reasonable to assume that the protective ability of the very large aggregates of Sterling FT rests partly on factors other than the conditions imposed by the Mie theory and perhaps simply these aggregates are effective because of their capacity to act as a geometric screen.

### Carbon Black-Antioxidant Relationship

In practical use, antioxidants are employed to decrease the tendency of polyethylene to undergo thermal degradation. In the three-component system, the chemical nature of the carbon black surface becomes quite important, and the relationship of this chemistry to that of the antioxidant has been the subject of many investigations.

Acidic carbon blacks of small particle size are actually mildly effective thermal antioxidants, but antioxidants are nearly always included in the preparation of compounds from these blacks to minimize the tendency of the polymer to undergo degradation during the processing stages.

Hawkins and Winslow's<sup>15</sup> findings are of particular interest, in that they report that carbon black in combination with thiobis(2-naphthol) acts synergistically to minimize the tendency of polyethylene to undergo thermal degradation. Even aliphatic thiols and disulfides which are not very effective in clear polyethylene are reported to give good protection in the presence of carbon black.

In contrast to this, Hawkins et al.<sup>16</sup> and more recently Crompton<sup>17</sup> point out that the amine antioxidants are adversely affected by carbon blacks of small particle size with acidic surface.

Certainly the relationship of the chemical nature of carbon black to the chemical nature of the antioxidant has been recognized as an important factor in formulating polyethylene compounds with improved resistance to thermal degradation.

In view of the great amount of attention given this aspect of performance, it is quite surprising that the present authors have been unable to find any data on the effect of the carbon black-antioxidant relationship on weatherability.

Our studies of three-component systems not only confirm the conclusions of previous investigators, but also provide tangible evidence that the rela-

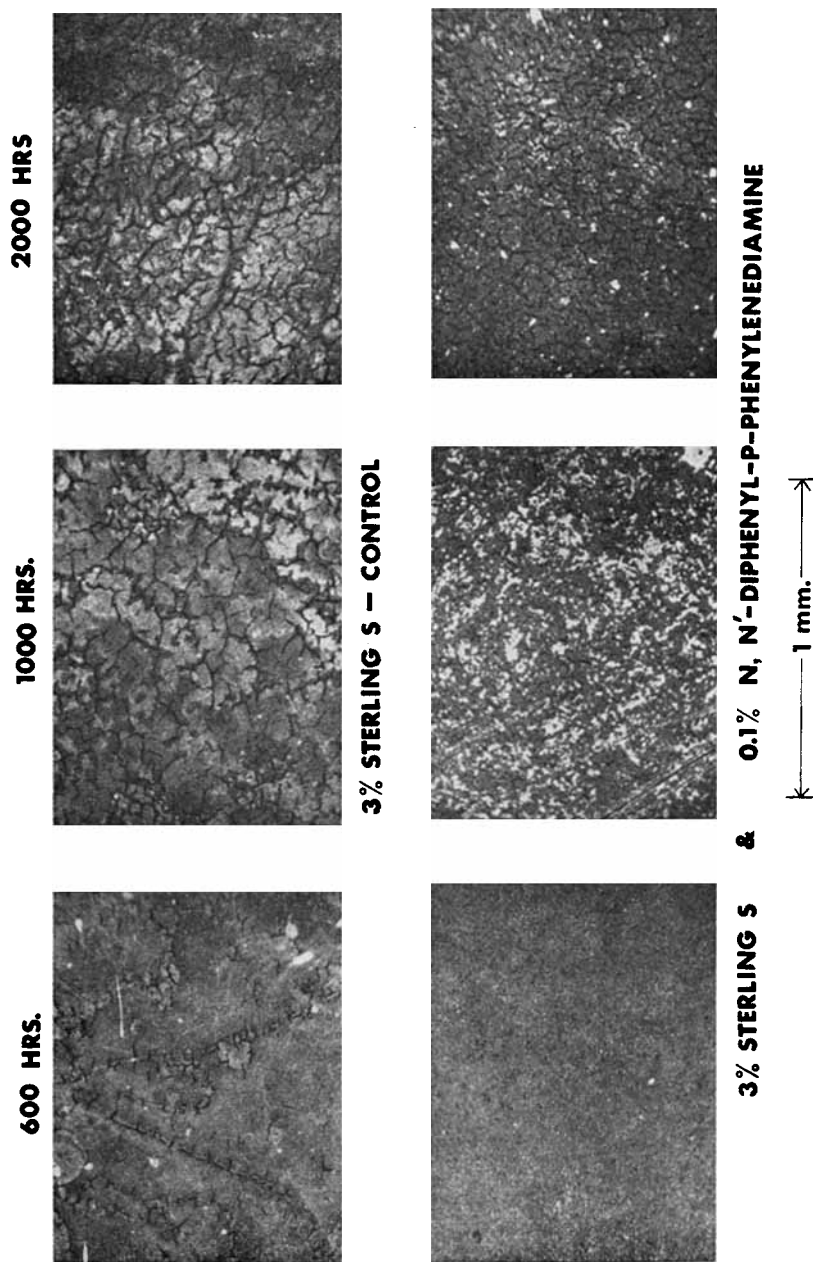


Fig. 11. Weather-Ometer aging of polyethylene.

tionship of the carbon black surface to the chemistry of the antioxidant has a significant influence on the weatherability (beyond that exerted by physical properties) as determined by accelerated aging of the compound. Although physical properties of the carbon blacks remain the predominant factor in three-component systems, it may be clearly shown that an amine type antioxidant enhances the weatherability of furnace carbons. Figure 11 illustrates this effect when Sterling S is used in the compound together with *N,N'*-diphenyl-*p*-phenylenediamine. Channel blacks do not show the same degree of improvement perhaps because the amine reacts with these acidic groups. Other types of antioxidants show marginal improvement at best. It is worth emphasizing that these results were obtained under conditions of accelerated aging in the Weather-Ometer.

Outdoor exposures have been in progress for four years, and the results at the present time are inconclusive. More time will be required to see whether the outdoor exposures will yield the results observed under conditions of accelerated aging.

### Mechanical Properties

Although carbon black is used in polyethylene at concentrations of 2–2.5% primarily to improve weatherability, the inherent behavior of small dimension particles in vehicle systems offers the possibility that other de-

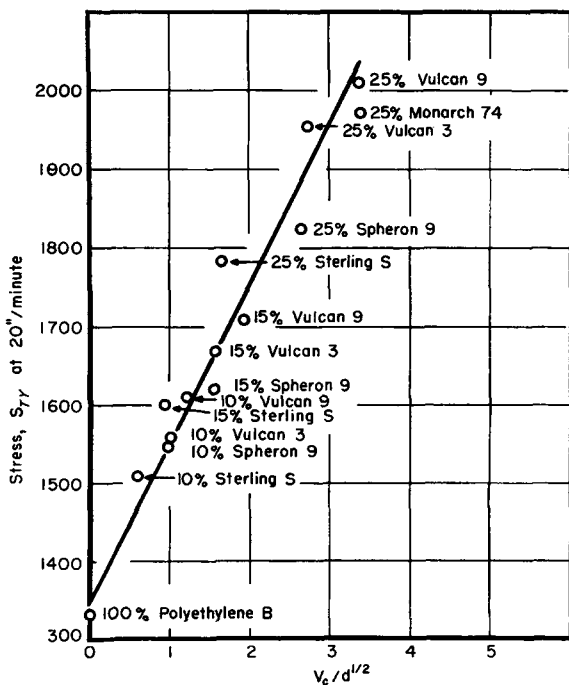


Fig. 12. Tensile yield vs.  $V_c/d^{1/2}$  for polyethylene compounds.

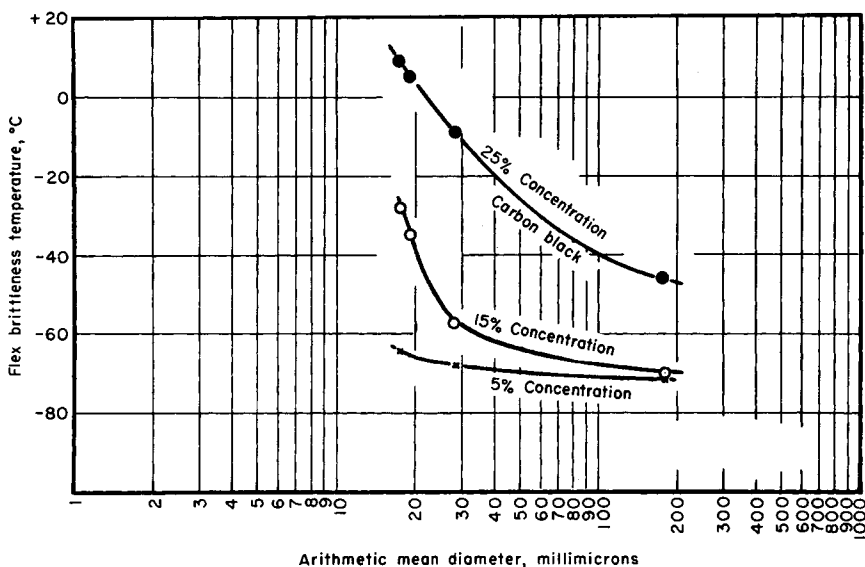


Fig. 13. Original brittleness temperature vs. particle size.

sirable properties can be obtained through proper formulation. To illustrate this point, various carbon blacks were dispersed into a low density polyethylene at 25% weight concentration. Part of the compounds were reduced to 10 and 15% concentration. Compounds were molded at approximately 65 mil thickness and tensile specimens were stamped. These were subjected to stress applied at 20 in./min. in a Scott tester. The stress at the draw point is referred to as the tensile stress  $S_{Ty}$ .

An empirical equation conveniently relates  $S_{Ty}$ , volume concentration, and primary particle diameter.

$$100(S_{Ty_f} - S_{Ty_0})/S_{Ty_0} = \% \text{ increase in } S_{Ty} = kV_c/d^{1/2}$$

where  $S_{Ty_f}$  is the tensile yield of filled compound,  $S_{Ty_0}$  is the tensile yield of polyethylene,  $V_c$  is the volume concentration of carbon black in the compound,  $d$  is the average particle diameter of the carbon black,  $k$  is a constant.

This relationship is shown in Figure 12, where the tensile yield or stress  $S_{Ty}$  is plotted against  $V_c/d^{1/2}$ .

Once again a property of compounds containing carbon blacks is seen to be dependent on the number and size of particles.

As in previous examples of this kind of relationship, the aggregate dimensions are probably the operative factor, but aggregate dimensions may be governed by primary particle dimensions. The nature of the surface chemistry does not appear to be a contributing factor in this relationship.

A complete investigation of the influence of carbon black on mechanical properties is outside the scope of this study; nevertheless the effect on tensile yield is significant and desirable for certain applications which

resist stress applied at fast rates. One such application is the use of polyethylene in pipe. Here, carbon black at higher concentrations would be expected to increase burst strength.

Whenever higher loadings of carbon blacks are used to obtain improved yield or burst strength or fatigue characteristics, care must be taken not to exceed the permissible specifications for the original brittleness temperature or flexibility of the end product. Figure 13 presents an idea as to the magnitude of the loss in original flex brittleness temperature as a function of the concentration and diameter of the carbon black used in such compounds.

The flex brittleness test determines the temperature at which a 65 mil strip  $1/2$  in. wide loses its ability to be flexed or, in terms of the test, breaks on bending rapidly around a  $1/2$ -in. diameter mandrel.

From Figure 13 it may be observed that up to 5% of any carbon black can be used without undue sacrifice in flex brittleness, and about 15% of some of the larger particle blacks may be used in applications where flex brittleness is less critical.

## CONCLUSIONS

The properties of a given carbon black polyethylene compound are dependent on both the physical and chemical characteristics of the black. The ability of a carbon black to impart protection to polyethylene by absorption of ultraviolet light appears to be largely controlled by its physical properties, protection seemingly a property dependent on the achievement of a sufficient number of optimum sized aggregates or units which must be well dispersed throughout the polymer mass. The technique of photomicroscopic examination of the surface of black polyethylene compounds for degree and type of crack development has proven to be an excellent method for comparing the relative ability of carbon blacks to impart protection to polyethylene exposed to ultraviolet radiation under natural and accelerated conditions. The examination of dispersions with the electron microscope has indicated that apparent discrepancies between the relationship of particle size to aging characteristics of certain blacks can be explained by the size and arrangement of the aggregates of these blacks existing in the compound.

The reactions of the polar groups on the surface of carbon blacks with polyethylene free radicals and/or antioxidants are important factors in the problem of thermal degradation. Similarly these factors also are important but to a lesser extent in the problems of photodegradation. The present study shows that the performance of nonpolar blacks is improved through the use of an amine type antioxidant as judged by accelerated aging studies.

Mechanical properties such as tensile yield and original brittleness temperature appear to be governed largely by numbers of particles per unit volume. Data on the ability of carbon black to alter mechanical properties as a function of particle diameter and concentration indicate that



higher concentrations than those used to obtain ultraviolet protection may be employed to enhance the burst strength and possibly fatigue characteristics of polyethylene pipe.

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### Résumé

On s'est efforcé d'élucider le rôle joué par différents types de noir de carbone incorporés dans du polyéthylène. On discute des propriétés physiques et chimiques des noirs de carbone et on détermine leur efficacité comme agent de protection du polyéthylène vis-à-vis des rayons ultraviolets. En première approximation c'est la taille des particules primitives du noir de carbone qui conditionne la résistance aux agents atmosphériques d'un composé donné. Comme le suggèrent les résultats, ceci serait dû au fait que le degré de protection aux ultraviolets dépend de la présence d'agrégats submicroscopiques et de leur distribution à travers la masse du polymère. On croit que la taille et la distribution de l'agrégat sont largement contrôlées par l'énergie de surface dépendant des dimensions des particules primitives. Les études des systèmes noir de carbone-antioxydant ont fourni des résultats en bon accord avec ceux de Hawkins et coll.; ceux-ci avaient trouvé que les noirs de carbone ayant une surface polaire présentaient un comportement synergétique en présence de substances antioxydantes de type organosoufré, ce qui augmentait fortement le temps nécessaire pour absorber une quantité donnée d'oxygène ou pour subir la dégradation thermique. Le présent travail montre que l'usage d'antioxydants contribue aussi à augmenter la résistance des polyéthylènes à un vieillissement accéléré. L'étude du vieillissement à l'extérieur du même composé est en cours mais il faut davantage de temps pour savoir si les antioxydants agissent de la manière trouvée dans les études de vieillissement accéléré. On discute de l'influence des noirs de carbone sur les propriétés mécaniques du polyéthylène et on présente des résultats montrant que, si on utilise pour la protection vis-à-vis des rayons

ultraviolets, un taux de noir de carbone plus élevé que d'ordinaire, on augmente considérablement le point d'étirement pour des tensions appliquées à assez grande vitesse. On pense que l'usage de concentrations modérément élevées de noir de carbone augmenterait les possibilités d'emploi du polyéthylène, par exemple dans la tuyauterie qui souvent ne résiste pas à une tension appliquée rapidement.

### Zusammenfassung

Eine zusammenfassende Untersuchung des Verhaltens verschiedener Russtypen in Polyäthylen wurde durchgeführt. Die physikalischen und chemischen Eigenschaften von Russen werden diskutiert und die Wirksamkeit verschiedener Russen als Ultraviolett-schutzstoff für Polyäthylen wird gezeigt. In erster Näherung zeigt sich, dass die primäre Partikelgrösse die Eigenschaft des Russes ist, welche grösstenteils die Witterungsbeständigkeit einer Mischung bestimmt. Die Ergebnisse lassen erkennen, dass dies darauf zurückzuführen ist, dass der Grad des Ultraviolett-schutzes von der Anwesenheit submikroskopischer Aggregate und ihrer Verteilung in der Polymermasse abhängt. Es wird angenommen, dass die Aggregatgrösse und -verteilung weitgehend durch die Primärpartikeldimension bedingte Grenzflächenenergie kontrolliert wird. Eine Untersuchung von Russ-Antioxydantensystemen lieferte Ergebnisse in Übereinstimmung mit denjenigen von Hawkins et al.; diese fanden, dass Russ mit einer polaren Oberfläche mit Antioxydantien vom Organoschwefeltyp ein synergistisches Verhalten zeigen und die zur Absorption einer gegebenen Sauerstoffmenge oder zum thermischen Abbau erforderliche Zeit stark erhöhen. Die vorliegende Untersuchung zeigt, dass die Verwendung von Antioxydantien auch die Fähigkeit von Polyäthylenmischungen zum Widerstand gegen Alterungsbeschleunigung verbessert. Alterungsversuche im Freien an denselben Mischungen sind im Gange, es ist aber eine längere Zeit erforderlich, um zu sehen, ob Antioxydantien in der durch die Untersuchungen bei beschleunigter Bewitterung angezeigte Weise wirksam sind. Der Einfluss von Russen auf die mechanischen Eigenschaften von Polyäthylen wird diskutiert, und Ergebnisse werden vorgelegt, welche zeigen, dass eine höhere Füllung mit Russ, als sie normalerweise zum Ultraviolett-schutz benützt wird, die Zuggrenze (Spannung beim Reisspunkt) bei relativ hoher Geschwindigkeit der angewandten Spannung stark erhöht. Es wird die Meinung ausgesprochen, dass die Verwendung mässig hoher Russkonzentrationen das Verhalten von Polyäthylen bei Anwendung als Röhren, wo oft ein Versagen bei rasch angewandeter Spannung auftritt, verbessern würde.

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