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Morphology of Aggregates: Particle Size and 'Structure' of Carbon Black from Electron Micrographs

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A new electron microscopical method for measuring carbon black particle size and primary aggregate shape parameters is given. The statistically sound conventions applied to the many steps in the procedure greatly reduce the subjectivity which was inherent in earlier microscopical methods for evaluating particle size and 'structure'. Results from this total concept approach to carbon black morphology provide detailed knowledge vital to the interpretation of results from other test methods. The technique should be applicable to other aggregated or anisometric materials.

The two parameters of carbon black morphology which are of greatest interest to the rubber industry are particle size and 'structure'. The term 'particle' has in the past carried the implication that discrete, spheroidal, dispersible entities exist in all grades of carbon black. However, recent electron microscopical studies of reinforcing grade blacks show conclusively that 'particles' are extensively fused together to form rigid irregularly shaped clusters or primary aggregates. Therefore, throughout this paper, the term particle shall mean that nodular portion of a primary aggregate which is discernible by virtue of its more or less spheroidal contour or by the fact that its connection to other portions of the aggregate is a 'neck' of smaller diameter than the particle *per se*.

Particle size is important to the rubber industry because it is the key parameter which determines the amount of external surface area per unit weight of black which is available for interaction with the rubber. In general, the smaller the particle size (*i.e.*, the higher the specific surface area), the greater the reinforcing ability of the black.

The term 'structure' was introduced (SWEITZER AND GOODRICH, 1944) to distinguish between blacks which, though similar in particle size and other parameters (surface area, surface chemistry and micro-structure), differed in the properties which they imparted to rubber and other systems. It has been generally accepted that 'structure' is related to the size and shape of the primary aggregates of carbon black. In this paper, the term primary aggregate means a cluster of particles or nodules fused together to form a rigid mass which is the smallest dispersible unit of carbon black. Also, the distinction has been made between *primary aggregates* and *secondary aggregates* (sometimes called agglomerates), the latter comprising more or less loose entanglements of two or more primary aggregates. 'Structure' (primary aggregate size and shape) is important mainly because of its effect on the extrusion shrinkage of rubber compounds and its effect on the modulus of rubber vulcanisates.

BACKGROUND

Particle Size Evaluation

Historically, carbon black particle size has been evaluated by electron microscope techniques, surface area techniques, measurement of optical properties such as jetness, X-ray small-angle scattering and by centrifugal sedimentation techniques. Unfortunately, all these techniques suffer from certain inherent limitations.

For example, the interpretation of surface area measurements is often complicated by the presence of micro-porosity. Also, there is at pre-

sent no way to obtain a particle size **distribution** from surface area data. Optical properties such as jetness, which can be evaluated quickly and precisely, do not give direct, independent information about particle size.

The most versatile techniques for particle size measurement are the electron microscope techniques. Measurements made from electron micrographs can be used to calculate d_n, the number average diameter, d_s, the surface average diameter, d_v, the volume average diameter and *S.A.*, the surface area of the black. Also, one may obtain a distribution of particle sizes from electron microscope methods and, as will be shown later, one may obtain (quantitatively) a variety of primary aggregate morphology parameters.

Ever since the early 1940's, the carbon black industry has been using the electron microscope as the primary tool for particle size measurement. An excellent review article (HESS AND FORD, 1963) provides much helpful background information on the development of electron microscope techniques for studying carbon black and carbon black-elastomer systems. Traditionally, we have made ruler measurements of apparent particle diameters from electron micrographs in the form of conventional photographic prints. More recently, some laboratories, including ours, have used a semi-automatic instrument (Zeiss Particle Size Analyser) for transmitted light measurements on translucent prints. This instrument is designed so that a round spot of light is projected onto the translucent print, the spot size is adjusted to match the area of a given particle, and the spot diameter is recorded in one of 48 categories. Thus, thousands of measurements may be made and accumulated in a matter of hours.

In some laboratories, particle size is estimated by visually comparing an electron micrograph of an unknown material to the micrograph of a standard black whose particle size had been determined previously by the Zeiss Analyser method. However, this expedient places heavy reliance on operator judgment and does not provide accurate information about particle size distribution.

Unfortunately, it has been shown (MEDALIA AND ROPER, 1963) that the reproducibility of results from the ruler method and the Zeiss Analyser method leaves much to be desired. Medalia and Roper conducted a large number of particle size measurements under various conditions and subjected their results to rigorous statistical analysis. They found that the precision of particle size measurement is comparable to the size differences between grades of carbon black. Thus, they concluded that there was no hope of discerning size differences between lots of a **given** grade, and little hope of distinguishing with confidence between **two** grades of black of slightly different particle size. During the course of that study, means were developed for calibrating the electron microscope very accurately (HECKMAN AND ROPER, 1962), photographic enlargements were made very accurately and reasonable precautions were exercised in sampling. Therefore, the low precision of the results was attributed to the variability in degree of dispersion from run to run and the high degree of subjectivity inherent in the processes of: (1) selecting fields to be photographed in the electron microscope, (2) selecting 'particles' for measurement on the finished micrograph and (3) applying criteria for discerning 'particles'. Of these three difficulties, the latter is by far the hardest to deal with because it is imposed by the nature of the material itself. Specifically, the 'particles' within the primary aggregate are so extensively fused together that it is sometimes very difficult to identify them and virtually impossible to measure them. The uncertainty in identifying particles due to fusion is compounded by the fact that while particles and aggregates are three-dimensional objects, their images occur as two-dimensional projections in conventional electron micrographs. Thus, portions of an aggregate which extend slightly above (or below) the object plane cast images which overlap in the plane of the micrograph. Consequently, one often sees aggregates, especially the larger ones, in which the considerable range in optical density adds to the difficulty of discerning and measuring particles *[Figure 1(a)]*. These major sources of error, inherent in earlier techniques, were eliminated or minimised in the new technique the description of which is given here.

EVALUATION OF STRUCTURE

In the past, several methods have been proposed to evaluate 'structure' or primary aggregate size and shape. Among these are compression methods, vehicle demand methods, light scattering methods and electron microscopical methods. However, as in particle size measurement, each of these techniques has shortcomings and limitations. Although results obtained by the first three methods (especially the vehicle demand methods) correlate reasonably well with rubber properties, they are capable only of giving average values. The only methods capable of giving **distributions** in aggregate morphology parameters are the electron microscopy methods.

According to ENDTER (1950), the chain structure of carbon black was first reported in 1939 by Von Borries and Ruska, while COHAN AND WATSON (1951), first attempted quantitative characterisation of structure. However, the chain concept of primary aggregate morphology, which these authors used, does not seem applicable to the cluster-shaped aggregates seen in electron micrographs of modern reinforcing grades of black. Other workers, including the present authors, have thought that they could observe differences between high and low structure blacks in the electron microscope. However, dispersion problems and subjective factors such as field selection have hampered previous attempts to use the electron microscope to distinguish qualitatively between blacks of varying structure.

During the earlier stages of their comprehensive study of carbon black morphology, the authors developed a new approach to the morphology of aggregates based on the dynamic parameters of their projected silhouettes (MEDALIA, 1967; MEDALIA AND HECKMAN, 1967) as shown schematically in *Figure 1(b)*. In simplest terms, this method consists of calculating unequivocally the central principal axes of the aggregate, represented by its silhouette, from the location of all points within it. These axes are drawn of lengths equal to four times the radii of gyration, and a radius-equivalent ellipse is drawn with these axes, as shown in *Figure 1(b)*. This treatment enables one to calculate three important aggregate morphology parameters:

Area (of silhouette): A

Anisometry (ANISO): K_A/K_B

where K_A and K_B are the larger and smaller radii of gyration about the central principal axes; and

Bulkiness (BULKY): $$\frac{\text{Area of ellipse}}{\text{Area of silhouette}} = \frac{4\pi(K_A/K_B)}{A}$$

The validity of derivation and significance of these aggregate morphology parameters were presented and discussed in an earlier paper on the general subject of 'Morphology of Aggregates' (MEDALIA AND HECKMAN, 1967).

The work which is described below was designed to accomplish two major objectives. The first objective was to eliminate or minimise subjectivity in field selection, aggregate selection, particle selection and particle size measurement; the second objective was to introduce a total concept of carbon black morphology, which includes both particle size and primary aggregate parameter measurement. The probability of attaining the second objective with accuracy is greatly increased because of the built-in requirement that every aggregate in the statistical sampling must be evaluated.

EXPERIMENTAL

Previous work has shown that within any given lot or sample of reinforcing black there are huge variations in aggregate size and shape and that the particle size values may vary by an order of magnitude. Since there are such large variations in parameters, we must make the necessary measurements and calculations on a large number of aggregates, if we are to characterise the entire sample of carbon black. This involves optimising dispersion, a statistically reliable method of selecting aggregates to measure, and a reasonably convenient way of carrying out the measurements and calculations. The steps required are outlined below.

1. Dispersion of Carbon Black into Primary Aggregates

The carbon black is dispersed in collodion (diluted 1:40 in ethyl acetate) by means of ultra-

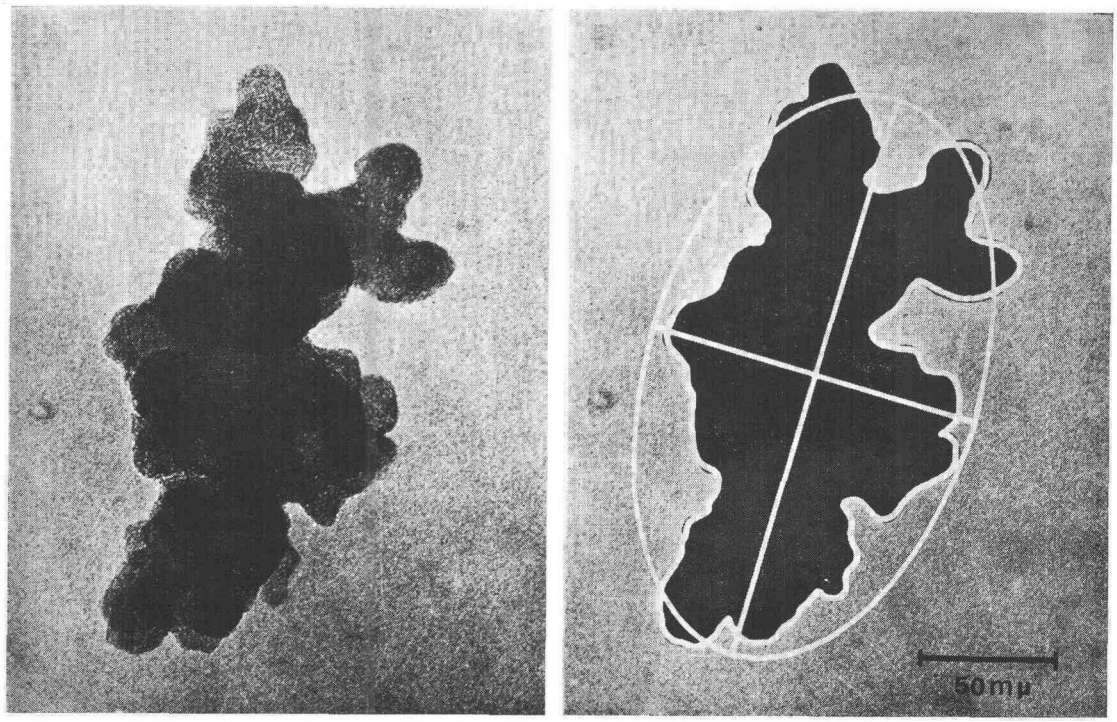

Figure 1(a). Carbon black primary aggregate (the large degrees of 'particle' fusion and the overlap of 'particle' images make particle characterisation difficult).

Figure 1(b). Silhouette of aggregate shown in Figure 1(a) *with schematic representation of its radius-equivalent ellipse superimposed.*

sonic energy. Typically, 4–6 mg of reinforcing grade carbon black is weighed into a 45 ml vial; 30 ml of diluted collodion is added; the vial is immersed in a water bath to avoid overheating; and an ultrasonic probe is inserted and run for five minutes with a power output of 75 watts at 20 kc/s. However, black concentration must be adjusted to take into account aggregate and particle size in order to keep the population (in the cast film) within acceptable limits. A standard microscope slide (1″ × 3″) is dipped in the suspension, drained of excess and dried. The edges of the cast film are scored, and the film is floated off on water and picked up on a bare 300-mesh electro-formed specimen grid. In some cases where the particle size is small, the floating film is picked up on carbon-coated grids and the collodion is washed away, thus improving the image quality of the resulting micrographs.

2. Electron Micrographs of Pre-selected Fields

In order to avoid operator bias, micrographs are taken of 13 grid openings (out of approximately 530 visible in the electron microscope) according to a pre-determined sequence which gives representative coverage over the entire grid. Each micrograph is taken in approximately the center of the grid opening. For reinforcing grades of black, micrographs are taken at approximately 20 000 × (with an RCA EMU-3F Electron Microscope) and printed at 168 000 ×. However, very small particle size blacks are taken at about 40 000 × while very large particle size blacks are taken at around 8 000 ×. It is

necessary sometimes to photograph more than 13 fields in order to have enough black to study. When this is necessary, extra fields are photographed on new grids in multiples of 13.

3. Selection of Aggregates for Measurement

Within each printed micrograph, a rectangle is inscribed whose borders are determined by the longest dimension of any of the aggregates visible. The rectangle is divided into quadrants, and each aggregate whose left-hand-most point is within the chosen quadrant is outlined and numbered for computer analysis. The upper left-hand quadrants of **all** the electron micrographs are handled in this way; if this does not give at least 200 aggregates, then the lower left-hand quadrants of **all** the electron micrographs are handled; and so forth. In most runs, at least 200 aggregates were measured.

In order to minimise reliance on operator judgment in distinguishing between overlapping and adjacent aggregates, we have established the convention that if two aggregates are separated by a distance greater than twice the width of the Fresnel fringe around a particle, they are considered to be separate. Although this convention accounts for most of the cases observed in practice, a small but significant fraction of the cases require further consideration. If a certain segment (or segments) of an aggregate consists of particles of significantly different size than the rest of the aggregate and it appears that the segment(s) is merely in point contact with the rest of the aggregate, they are considered separate aggregates. This step is taken because of the long-standing observation that particles within a given aggregate tend to be about the same size.

The final step in this procedure is to assign an average particle size to each aggregate. This is done by measuring (by ruler) all measurable particles within the aggregate and taking the average. The average particle size of each aggregate is recorded and sent on for computation. This procedure is tantamount to evaluating around 20 000 particles per run.

4. Digitising of Outlines and Computation

The outline of each selected aggregate is traced by an operator using an electronic pencil follower device which digitises the position of the co-ordinates onto paper tape at a rate which keeps up with the maximum speed with which the operator can conveniently trace the outline. Provision is made for cancelling errors, and for tracing and digitising void spaces in an aggregate.

A computer programme was developed which accepts the average particle size of each aggregate, the digitised co-ordinates of the outline and calculates the co-ordinates of the points (on a 0.5 mm grid) which lie within the outline. The programme then computes the particle size data and calculates the value of the aggregate morphology parameters of this silhouette in accordance with the equations given previously (MEDALIA, 1967). The co-ordinates of the silhouette, along with those of the central principal axes, are stored on a tape for subsequent display. The particle size data and the morphology parameters of each aggregate are stored (on tape and punched cards) for statistical analysis at the end of the run.

5. Comparison of the Computer Output with Electron Micrographs

In view of the number of steps involved, it seemed advisable to check the final results against the original data (*i.e.*, the electron micrographs). To do this, the silhouette of each aggregate is displayed on a cathode ray screen and automatically recorded on microfilm. The central principal axes are also displayed, superimposed on the silhouette, and grid squares are drawn corresponding to 15 mm on the micrograph The microfilm is examined by means of a microfilm reader; the silhouette of each aggregate is compared visually with the original electron micrograph, and its area and other parameters are compared with those listed in computer output. The operator can tell at a glance if any gross errors have been committed, and if the parameters look reasonable. In addition, spot checks are made by ruler measurement of the dimensions of the silhouette *versus* those of the aggregate micrograph. When errors are found, the aggregates in question are re-digitised and the new data are used in place of the old in computing the final statistical parameters.

TABLE 1. CARBON BLACK MORPHOLOGY PARAMETERS FROM ELECTRON MICROGRAPHS

Black	Particle size parameters (mμ) Range	d_n	d_s	d_v	d_s/d_n	Range factor	S.A. m^2/g	Aggregate morphology parameters ($\mu^2 \times 10^3$) Area–Range	WAAA	ANISO	BULKY
V6H (N242)	11–38	22	24	25	1.09	3.5	136	0.50–305	61	1.75	1.18
V6 (N220)	12–42	22	26	28	1.18	3.5	127	0.50–183	45	1.75	1.24
R660 (N219)	13–43	24	27	28	1.13	3.3	121	0.32– 88	15	1.66	1.11
V3H (N347)	12–44	27	31	33	1.15	3.7	104	0.32–247	76	1.78	1.22
V3 (N330)	12–66	32	37	39	1.16	5.5	88	0.43–129	38	1.74	1.14
R300 (N326)	12–50	26	31	32	1.19	4.2	106	0.43–181	39	1.66	1.10
Sph 6 (S301)	12–50	32	35	36	1.09	4.2	93	0.25– 92	27	1.80	1.15

RESULTS AND DISCUSSION

The particle size and aggregate morphology parameters which were derived from measurements made according to this new technique are given in *Table 1*. Since refinements in technique are still being made, these results should be considered preliminary. A brief description of the blacks studied is given below, including the A.S.T.M. designation in brackets. The first group consists of three ISAF types of varying structure: Vulcan 6H(N242)—High Structure (experimental type), Vulcan 6 (N220)—Medium Structure, and Regal 660 (N219)—Low Structure. The second group consists of three HAF types: Vulcan 3H (N347)—High Structure, Vulcan 3 (N330)—Medium Structure, and Regal 300 (N326)—Low Structure; finally, one rubber grade channel black was studied: MPC–Spheron 6 (S301). Particle sizes are given to the nearest milli-micron (mμ) and aggregate areas are given in square microns $\times 10^3$ ($\mu^2 \times 10^3$).

In *Table 2*, three sets of results by the new technique (obtained on current lots of black designated NEW) are compared to old ruler results [obtained by MEDALIA AND ROPER, (1963) on other lots of black designated OLD].

Many interesting trends are shown in *Table 1*. First, particle size *(i.e., d_n, d_s, d_v)* does not overlap between the ISAF and HAF types. Second, particle size (within a given sample) by the new technique varies over a small range as indicated by the range factors of between 3.3

TABLE 2. COMPARISON OF PARTICLE SIZE VALUES BY OLD AND NEW METHODS

Black	Method	Range (mμ)	d_n (mμ)	d_s (mμ)	d_s/d_n	Range factor	S.A. m^2/g
V6	OLD	5–60	24	33	1.40	12.0	97.5
V6	NEW	12–42	22	26	1.18	3.5	133.5
V3	OLD	5–65	28	36	1.28	13.0	90.6
V3	NEW	12–66	32	37	1.16	5.5	87.6
Sph 6	OLD	7–56	25	31	1.24	8.0	105.1
Sph 6	NEW	12–50	32	35	1.09	4.2	92.5

and 5.5. Finally, the major difference between blacks of varying structure (within a given grade) is in aggregate size as indicated by the weight average aggregate area (WAAA). However, it should also be pointed out that low structure blacks are slightly lower in anisometry (ANISO) and bulkiness (BULKY) than medium and high structure blacks.

Several significant findings are recorded in *Table 2*; however, it must be kept in mind that the old and new techniques were applied to different lots of black. There are no startling differences between *average* particle size by the old ruler method and the new method. The large differences in particle size **range** (between old and new method) are attributable to the fact that in the new method, particle size is averaged within a given aggregate; thus, extremes in particle size are sharply reduced. In the old technique, on the other hand, operators tended to select for measurement smaller particles at the periphery of aggregates or those which were part of small-particle aggregates. This practice tended to give biased particle size results in which both average size and size distribution were shifted toward the small end of the scale. Thus, the authors think that the 'weighted' particle size range and the smaller d_s/d_n ratio given by the new technique are considerably more meaningful than the results given by earlier methods.

The surface areas *S.A.* by both old and new techniques are computed on the assumption that the 'particles' are discrete spheres of diameter d_s. Since few, if any, discrete spheroidal particles are ever seen in reinforcing blacks, we know that the calculated surface area is only an approximation of the real value. According to rough calculations, this approximation could be high by 5 to 20%, depending on the model of the inter-particle connection (*i.e.*, cylindrical, common plane, etc.) used in the calculation. Since each reinforcing grade of black studied showed a tremendous variety of inter-particle connections, no acceptable correction factor for the calculated surface area has been devised as yet.

In conclusion, the authors would like to give their appraisal of the technique in its present state of development. Although they have exercised every means at their disposal to eliminate or minimise subjectivity throughout all the steps in the procedure, they must point out that there is still a certain amount of judgement involved in particle size measurement, due to the previously described complications in interpreting electron micrographs. However, having made particle size measurements by several techniques over the years, the authors are confident that the new method, by virtue of its greatly increased objectivity and its requirement that each aggregate be examined as a whole, has produced the most realistic particle size values obtained to-date. An added measure of confidence in the new results is derived from the fact that they are in good qualitative agreement with corresponding standard analytical results. For example, jetness and surface area values agree qualitatively with particle size and calculated surface area while, with one exception, the aggregate morphology results are in agreement with vehicle demand (DBP) results.

The new knowledge provided by the total concept of carbon black morphology should be of considerable value in predicting properties imparted to rubber and other systems. Also, a prior knowledge of morphology should be useful in the interpretation of results from other physical methods of analysis, such as light scattering, small-angle X-ray scattering, centrifugal sedimentation and the like. Finally, this technique should be applicable to the characterisation of other colloidal materials of aggregated or anisometric morphology.

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DISCUSSION

Chairman: Dr. W. L. Resing

Dr. C.E. Scott asked about the comparative costs and time involved between the new method and the older Zeiss technique for estimating the morphological characteristics of carbon black. Dr. Heckman said that the Zeiss technique required four times as many man-hours in the laboratory as needed for the new method, which was also designed for adaptation to data-analysis by computer. The older estimation technique required even more time than the Zeiss or the electron micrograph methods.

Replying to Dr. B. Saville, Dr. Heckman explained the term 'anisometry' as applied to aggregates. When the operator digitises the outline, the X–Y co-ordinates of all the points that lie within the aggregate are calculated on a half millimetre grid system. From this the radius equivalent to four times the radius of gyration of the particle is computed by the formula derived by Dr. Medalia. The anisometry value is the ratio of the larger to the smaller radius.

Dr. A.A. Watson asked if the complex aggregates broke down into much simpler particles on mixing the carbon black with rubber. Dr. Heckman said the substantial reduction in size of the aggregates on mixing with rubber had been measured by electron microscopy, although the results were surprisingly different in some aspects from those obtained previously by DBP or oil absorption studies. These results were now being prepared for publication.