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by

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# Role of Carbon Structure in the Reinforcement of Rubber

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[At a meeting held in Stockholm on 26th and 27th November, 1954, arranged by the Swedish Institute of Rubber Technology, the following paper was read by Dr. Sweitzer.]

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## SUMMARY

*During their formative stage carbon black particles, by partial fusion during collisions, tend to form elongated chains of particles of varying extent and permanence. This three-dimensional chain development has been designated carbon structure. The fragile portion of this structure is lost during processing of the dry black. The more permanent portion of this structure will persist in varying degree during processing in rubber and will affect the properties of these compounds in a manner akin to that associated with anisotropic particles. In unvulcanised compounds increasing carbon structure results in higher viscosity and greatly improved extrusion properties. In vulcanisates, increasing carbon structure results in higher modulus, improved abrasion and enhanced roadwear. The hysteresis penalties incurred through the use of carbon structure to develop higher modulus are mild compared with those encountered when alternative means are employed. Carbon blacks with varying degrees of persistent structure, in the more popular size ranges, are available to the rubber compounder for applications requiring improved extrusion, higher modulus and such related benefits associated with the carbon structure effect.*

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## INTRODUCTION

For years, prior to the confirmation of the structure property in carbon blacks by the electron microscope, it was recognised that significant differences existed among carbon blacks with respect to their ability to alter the stiffness of natural rubber compounds. These differences could not be ascribed satisfactorily to fineness and various investigators

speculated on the probable cause of these effects. Perhaps Cranor<sup>1</sup> in 1925 was the first to draw attention to these differences, observing that lamp black produced rigidity in tyre treads but with a lack in ultimate tensile strength and energy. In 1926, Wiegand<sup>2</sup> suggested that this stiffening effect of lamp black might be due to the shape of its particles, pointing out the analogous effect of fibrous non-carbon pigments. Spear and Moore,<sup>3</sup> Goodwin and Park,<sup>4</sup> Parkinson,<sup>5</sup> and others speculated on the probable explanation for this stiffening effect of lamp black, the sum of their conclusions being that some sort of particle anisotropy must be assumed to account for this behaviour of lamp black.

With the release of the first electron microscope pictures of carbon black in 1940,<sup>6</sup> the development of the present concept of carbon structure followed rapidly. The electron microscope, which made possible the direct observation of the ultimate particles of carbon black, partially confirmed previous speculations. Although the ultimate particles were spheroidal, they were observed to be fused into elongated chains of varying length. There followed in 1941<sup>7</sup> the announcement of structure as a fundamental property of carbon blacks. Carbon structure was defined as a more or less rigid or permanent three-dimensional carbon network system, present in all carbons at the time of manufacture, and varying in the permanence or persistence of these fused chains in the rubber compound.

Extensive evaluation of the carbon structure effect in rubber has followed. To-day carbon structure, together with particle size or surface and surface chemical activity, are rated as the three important properties of carbon black influencing rubber reinforcement. They have been referred to as the Three Building Stones<sup>8</sup> in the carbon reinforcement of rubber. The role of structure will vary with the polymer and the end-use of the reinforced compound, but in the broadest terms its most significant role is one of enhancing viscosity in both the unvulcanised and vulcanised rubber compounds. This story of carbon structure and its effects on rubber properties is the subject of this paper.

### *The Nature of Carbon Structure.*

Although some investigators consider structure to be a flocculated state, consisting of strings of carbon particles held together by physical forces, the evidence seems unmistakable that structure consists of chains of carbon particles fused together by carbon linkages or necks, in other words, held together by chemical bonding. The presence of these necks was first demonstrated by Ladd<sup>9</sup> and subsequently confirmed by Watson.<sup>10</sup> These fused links or necks will vary in number, in size and in strength for the different carbons, depending on the process of manufacture. Examples of original carbon structure as revealed by the electron microscope are presented in Figure 1. The two carbons represent extremes in structure, the thermal gas process Thermax with a low degree of structure develop-



ment, the Germantown oil process lamp black with a high degree of structure development. The numerous rod type linkages are evident in Thermax with the chain length short, whereas with lamp black the fused junctions are generally thick with the chain length long.

A plausible mechanism for the development of carbon structure during manufacture is offered by the tentative *droplet theory* of carbon formation. This picture fits in well with the theory that the immediate precursor to the carbon particle in any type of carbon producing flame is a highly viscous liquid droplet, consisting of high molecular weight hydrocarbons, formed as the result of successive condensation and dehydrogenation reactions occurring during the pyrolytic decomposition of the gas or oil raw material. As pointed out by Grisdale,<sup>11</sup> it is only necessary to postulate collisions between these viscous droplets to explain the fused reticulate chain structure of carbon blacks. The size of the carbon particles will depend on the size of these liquid droplets, whereas the degree of structure will depend on the number of collisions and the conditions under which the collisions take place.

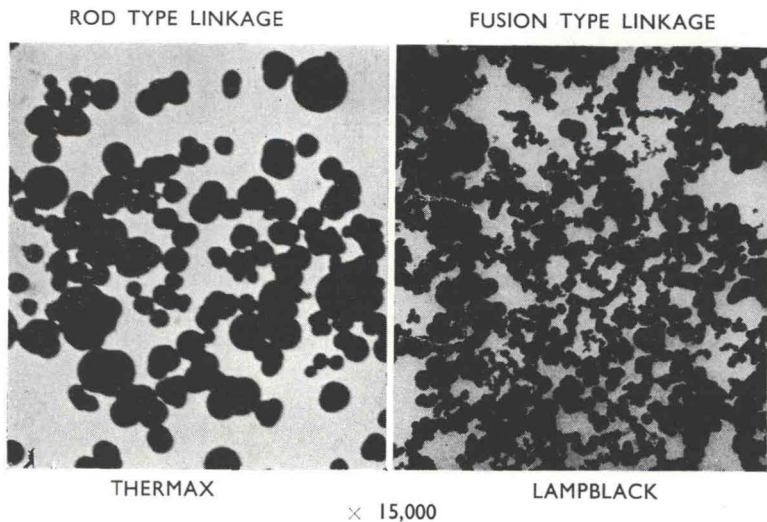
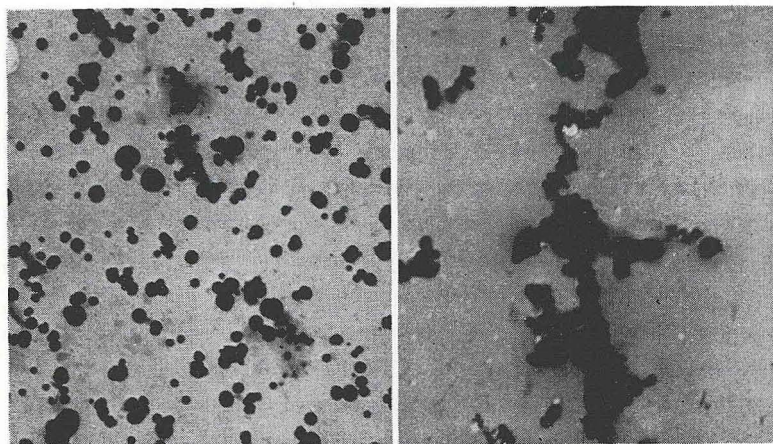


FIG. 1.  
Original structure.

### *The Persistence of Carbon Structure.*

Immediately after formation, all carbon blacks are typified by an extreme state of fluffiness. In the processing of these fluffy carbons at the plants by agitation, conveying, densing, and pelletising, the greater part of this fluffiness is lost. This loss is associated in part to the release of the aggregative physical bonds and in part to the breakdown of a fragile type of structure, present in varying degree with all carbons at the time of formation as shown in Figure 1. In the subsequent mixing or mastication of the densed or pelletised carbon black in rubber a further loss in structure occurs. It is the structure retained after all these processing steps that determines the final role of carbon structure in the rubber compound.

#### EXTREMES IN STRUCTURE PERSISTENCE



P-33

× 15,000

LAMPBLACK

FIG. 2.

Extremes in structure persistence.

The loss of fragile structure during processing of the dry carbons at the plants can be followed by density measurements, although such tests are subject to error owing to the difficulty in maintaining a constant level. A simple test employed in our laboratories is to measure the capacity of the carbon to retain a liquid which is added without agitation. Employing this method the loss of structure in going from the fluffy to the beaded state can be followed readily as demonstrated in Figure 3. It is noted

that although all the carbons lost structure the differences present in the fluffy state persisted in the densed or beaded state.

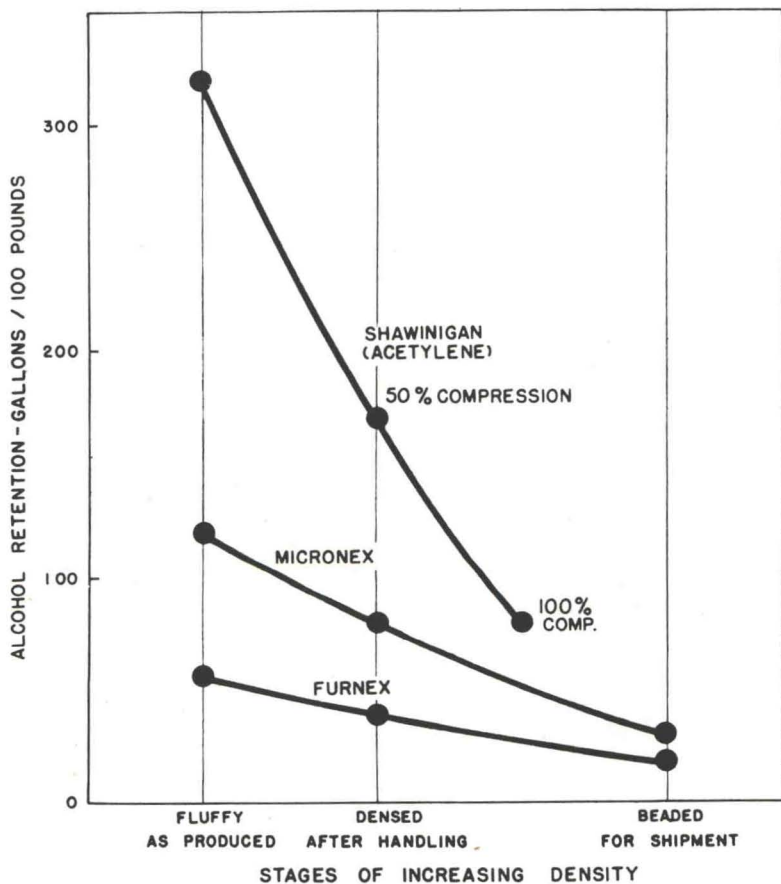


FIG. 3.

Loss of fragile carbon black structure during manufacture.

In the processing of the densed or beaded carbon black in any vehicle there is a further loss in structure. An indication of the structure loss, or conversely the structure persistence, suffered by two carbons representing



extremes in structure level, in processing from the original fluffy state to the final dispersed state in a vehicle, is provided by comparing Figure 2

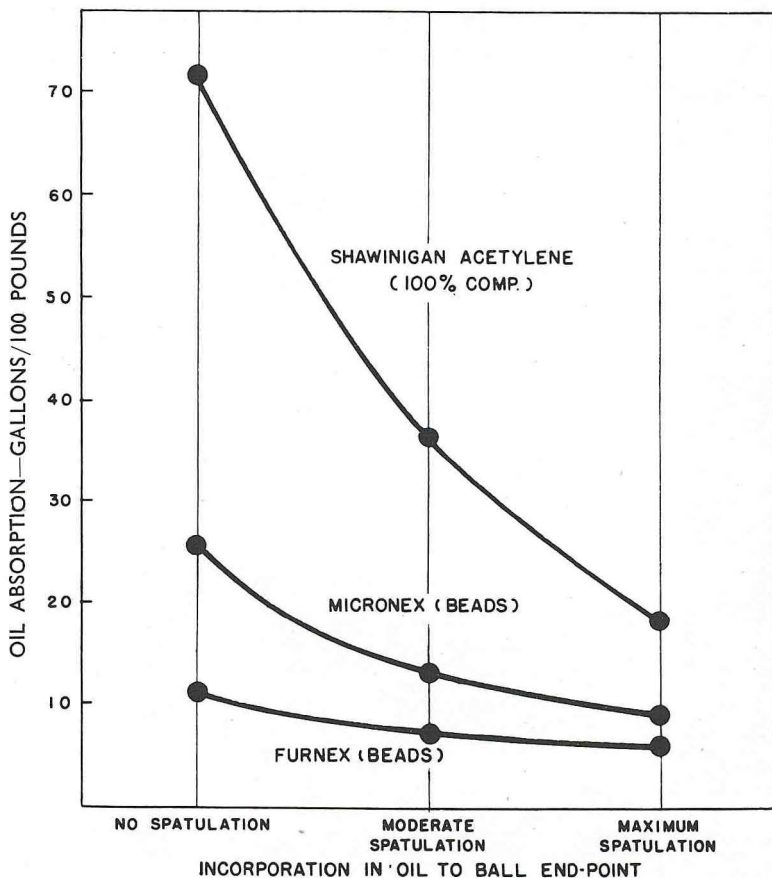


FIG. 4.  
Loss of carbon structure by spatulation.

with Figure 1. The thermal carbon has been broken down to substantially discrete isotropic particles whereas the lamp black shows persistent elongated groups of pronounced anisotropy. A measure of the structure loss

associated with the severity of dispersion procedure in a vehicle is demonstrated by the graphical record in Figure 4. In this test the most dense

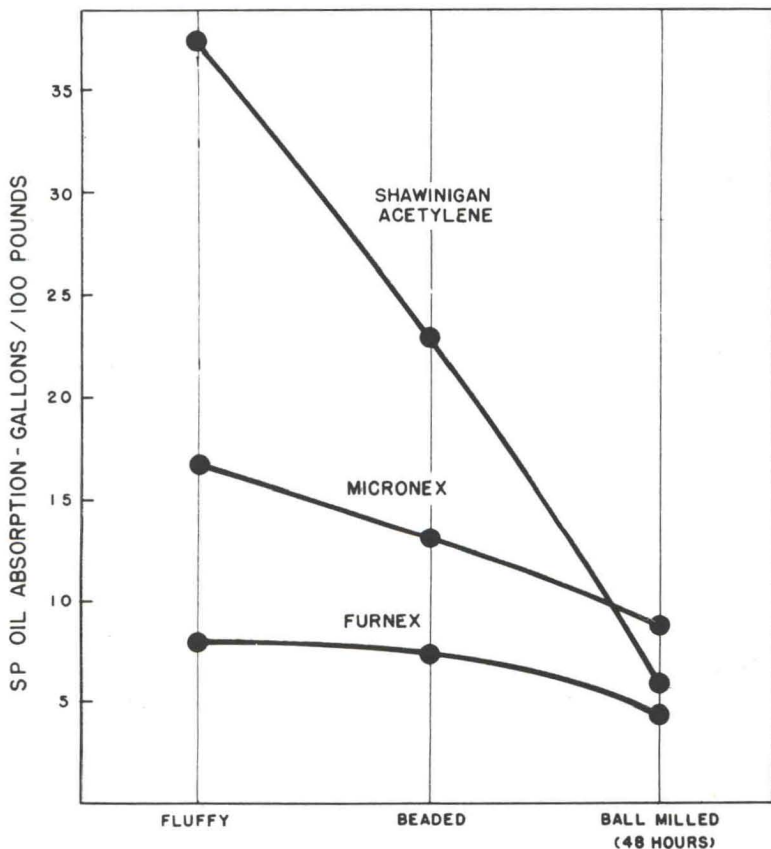


FIG. 5.  
Complete destruction of structure by dry ball milling.

carbons employed in Figure 3 were tested for oil absorption, using a constant end-point of a coherent ball, but increasing the severity of the manipulation to reach this end-point. In the first step shaking alone was

involved, in the second step spatulation of a moderate nature was employed, whereas in the final step maximum spatula pressure was used in spatulating the carbon and oil. All the carbons lost structure, but again the differences present initially persisted after maximum spatulation. It is of interest to note that the moderate spatulation step employed in Figure 4 was adopted as the procedure in the standard stiff paste oil absorption test described by Sweitzer and Goodrich in 1944.<sup>12</sup> This test, it has been demonstrated, provides the closest approximation to structure persistence in rubber, with differences given by this test correlating best with changes in the viscous properties of rubber compounds. In the light of these experiments there can be no rigid distinction between fragile and permanent structure. It is probable that with all carbons there is a graduated degree of structure permanence, the particular level at which this permanent structure persists in rubber or any other vehicle determining the structure effect.

Prolonged ball-milling of dry carbon black apparently destroys structure completely, as evidenced by the results presented in Figure 5. Oil absorption of the ball-milled carbons reaches low levels, with the values now associated with particle size rather than structure, as indicated by the value for Shawinigan lying below that of Micronex. The stiff paste oil absorption test destroys most of the fragile structure in standard rubber carbons, as shown by the results for Micronex and Furnex (fluffy versus beaded). Although ball-milling destroys all structure, direct compression such as employed in dense packaging fails to go beyond the effect provided by moderate spatulation as shown in Figure 4.

#### *The Measurement of Carbon Structure.*

Unquestionably the ideal measure of carbon structure would be *shape factor* values for the carbon black as dispersed in rubber, with shape factor providing an average length/width value for the carbon in its dispersed state. Cohan and Watson<sup>13</sup> have discussed shape factor for undispersed carbon but it is evident that such values would bear only the broadest relationship to the dispersed state of the carbon in rubber.

The electron microscope has provided the means for classifying broadly the degrees of structure formed within the family of carbon blacks, and such a classification by Ladd and Wiegand<sup>9</sup> is as follows:

Non-Structure	..	..	MT, FT
Normal Structure	..	..	EPC, FF
Intermediate Structure	..	..	SRF, HMF
High Structure	..	..	LB, Acetylene

It is evident that, although helpful, this broad classification fails to produce the degree of distinction required for precise interpretation of rubber data. The greatest value in Ladd's classification is the *normal* rating for the channel and fine furnace (FF) blacks, based on identical length for the permanent particle chains, and called normal because

channel blacks have been the industry standards for years. Employing this normal rating it was possible to devise a simpler and more satisfactory means for rating structure.

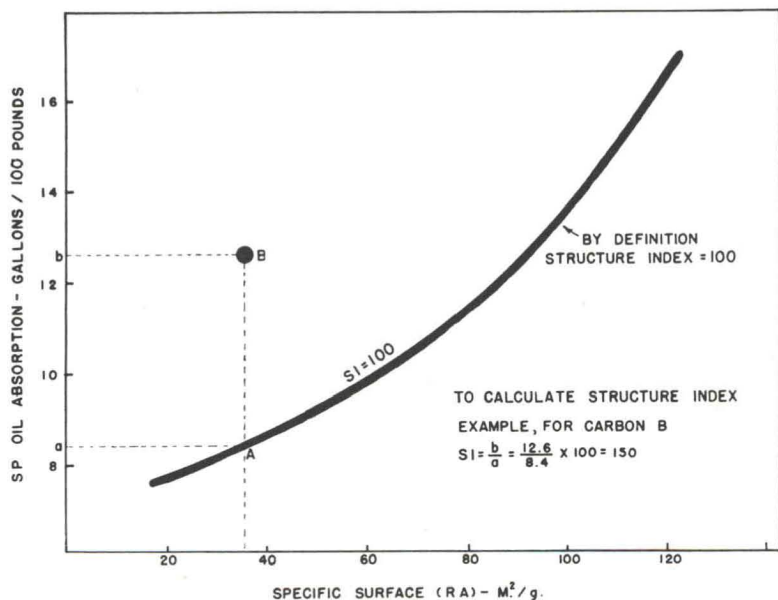


FIG. 6.

Relationship between oil absorption and fineness for normal structure blacks.

By plotting stiff paste oil absorption values against particle size or surface for these *normal structure* carbons, an oil absorption curve is obtained for carbons of varying particle size at constant structure persistence as shown in Figure 6. This *normal structure* curve is defined arbitrarily as *structure index* of 100. *Structure index* values for carbons with oil absorption values lying above or below this normal curve are calculated by factoring in terms of the normal as demonstrated in Figure 6. Hence *structure index* values above 100 indicate a degree of structure persistence greater than the normal carbons, by the percentage derived, in terms of increased stiffening effect in oil. Admittedly structure indices so derived are approximations but in the absence of valid shape factor or anisotropy data they do provide the best indication of carbon structure persistence in rubber compounds.



In the derivation of structure index values for carbon blacks it is most important that valid fineness or surface area values be assigned to these carbons. In the earlier development of *structure index*<sup>12</sup> the fineness scale

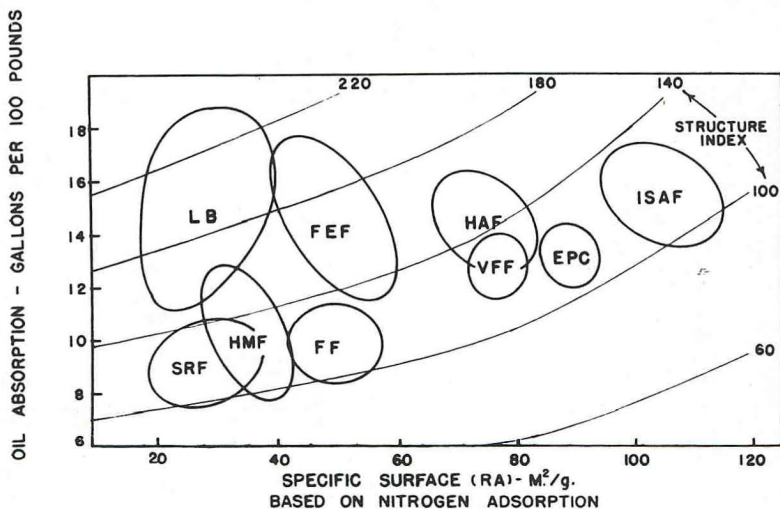


FIG. 7.

Dimensional classification of rubber carbons.

employed was specific surface as calculated from electron microscope diameter measurements—jetness or blackness was generally substituted as this property of the carbons was found to correlate well with electron microscope diameters. Recognition of the fused nature of the carbon to carbon attachments suggested that these electron microscope surface areas could be in error on the high side, by an amount determined by the unavailable surface at these fusion junctions, as the practice in these measurements is to confine readings to full diameters. Surface areas calculated from nitrogen adsorption measurements by the Brunauer-Emmett-Teller (BET) method<sup>14</sup> confirmed this error, as surface area values for some carbons were appreciably less than those calculated from particle diameter measurements. However it was also shown that total surface area values obtained by nitrogen or iodine adsorption could be on the high side by an amount determined by the particle pore surface that was available to nitrogen but not to rubber. On the basis of these observations the specific surface values previously assigned to carbon blacks have been revised to values considered more in accord with the surface available for rubber reinforcement. These revised values, based sub-

stantially on nitrogen adsorption surface area measurements, have been employed throughout this paper, with the designation *specific surface (R.A.)* on the graphs referring to *rubber available surface*.

*Classification of Rubber Carbons by Fineness and Structure.*

The foregoing discussion reveals that fineness must also be considered in assessing the role of structure, as greater fineness at a constant structure level as well as higher structure at a constant fineness level both lead to increased oil absorption or stiffening effects. By using a co-ordinate system with oil absorption as ordinate and the revised specific surface values as abscissa, the dimensional boundaries for the family groups of rubber carbons can be plotted as set forth in Figure 7. Structure levels, in terms of *structure index*, can also be shown. A more specific classification is shown in Figure 8 for typical representatives from these family groups. The surface and structure factors employed in the following section of the paper were derived from this classification.

The essential dimensional and chemical properties for the carbons plotted in Figure 8 are presented in Table I. Several observations of

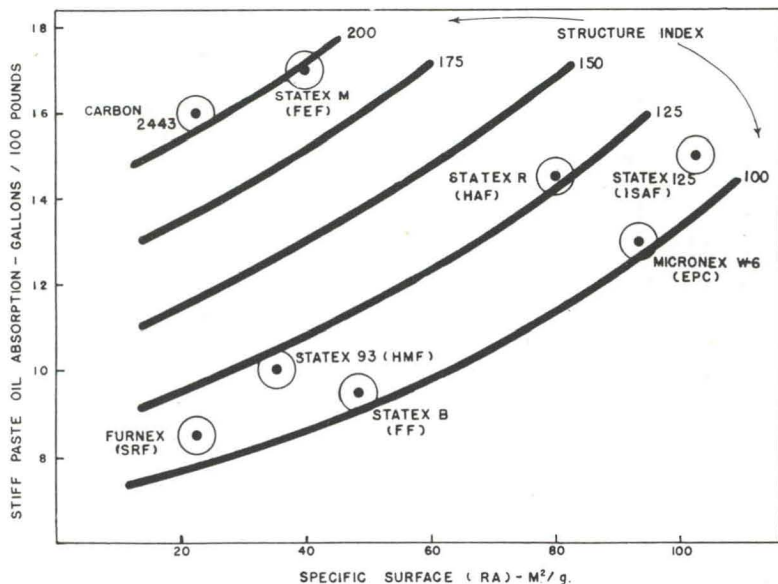


FIG. 8.  
Dimensional classification of rubber carbons.

TABLE I

## DIMENSIONAL AND CHEMICAL PROPERTIES OF RUBBER CARBONS

Carbons										
Grade .. .. .	2443	Furnex	Statex 93	Statex M	Statex B	Statex R	Statex 125	Micronex -6		
Class .. .. .	—	SRF	HMF	FEF	FF	HAF	ISAF	EPC		
Raw material ..	oil	gas	gas-oil	oil	gas	oil	oil	gas		
Process .. .. .	furnace	furnace	urnace	furnace	furnace	furnace	furnace	channel		
Dimensions										
Colour surface, M <sup>2</sup> /g. (1)	27	31	45	45	63	67 (4)	80 (4)	89		
N <sub>2</sub> surface, M <sup>2</sup> /g. ..	22	22	36	40	49	80	103	103		
Surface (RA), M <sup>2</sup> /g. (2)	22	22	36	40	49	80	103	94		
Oil absorption .. ..	16.0	8.5	10.0	17.0	9.5	14.5	15.0	13.0		
Structure index (3) ..	210	110	120	200	105	135	115	100		
Chemical Properties										
% volatile .. .. .	0.5	0.5	0.5	1.0	0.5	1.0	1.5	5.5		
pH .. .. .	9	8	9	9	9	7	8	5		
% extractable .. ..	0.05	0.05	0.10	0.10	0.05	0.05	0.05	0.01		

Notes.—(1) Based on colour—E.M. surface correlation.

(2) Based largely on nitrogen surface.

(3) Calculated to nearest multiple of 5.

(4) These carbons fall down in Colour—E.M. correlation.

E.M. values were 98 and 125 M<sup>2</sup>/g. respectively.

interest might be made. The gas blacks tend to be in the normal structure index band, with oil absorption increasing with fineness. The oil blacks, on the other hand, tend to fall within a more or less constant oil absorption level, with structure decreasing as surface area increases.

#### THE ROLE OF CARBON STRUCTURE IN RUBBER

Following the electron microscope confirmation of the structure dimension in carbon black, various investigators demonstrated the effect of this structure on the behaviour of rubber compounds and speculated on the probable mechanism involved. Wiegand in 1944<sup>15</sup> discussed the role of carbon structure in enhancing the modulus of GR-S compounds and questioned whether these networks of carbon function as fibers when aligned through the stretching of the non-crystallisable GR-S. Sweitzer and Goodrich in the same year<sup>12</sup> reviewed the carbon structure effect in Hevea and GR-S and showed that stiffness properties were enhanced in both polymers by structure carbons, with tensile and energy on the other hand depressed. Parkinson in 1945<sup>16</sup> reported that modulus had a high dependence on carbon structure, with abrasion resistance slightly modified by the degree of structure formation. Fineness was considered the dominant factor in tensile strength, tear resistance and resilience. Braendle *et al.* in 1948<sup>17</sup> discussed the importance of carbon structure in improving the properties of GR-S and visualised such carbons as very fine fibers to explain their effects in processing. In subsequent papers by Dannenberg and Collyer,<sup>18</sup> Parkinson,<sup>19</sup> and others this role of carbon structure was further delineated.

For a more precise interpretation of the role of carbon structure in rubber compounds there was need for a better understanding of the nature of structure, for a quantitative rather than a qualitative expression of structure level, and most importantly for a greater variety of structure carbons. With the introduction of new structure furnace oil carbons in recent years, and with the improved methods for evaluating structure levels, the essential basis for this more rigid analysis of the carbon structure effect in rubber has been made available.

#### *The Approach Employed.*

In the analysis that follows, the approach employed has been empirical rather than theoretical and graphical rather than tabular. Rubber property data were secured for natural rubber (NR) and low-temperature GR-S (LTP) compounds, by weighting and averaging all available test results from the laboratory records, in which compound, processing method and temperature, carbon loading, and other possible interfering factors were identical or substantially equivalent. Details of compound and procedure involved are set forth in Table 2.



TABLE 2

	COMPOUND, MIXING AND CURING DATA				
	Natural rubber compounds		Low temperature GR-S compounds (LTP)		
	Furnace	Channel	Furnace	Channel	
Smoked sheets	100	100	LTP .. ..	100	100
Carbon black ..	50	50	Carbon black	50	50
Zinc oxide ..	3	3	Zinc oxide ..	3.5	3.5
Stearic acid ..	3	4	Stearic acid ..	2	2
Pine tar ..	2	2	Paraflex ..	3	3
BLE powder ..	1	1	Circosol 2XH	5	5
Vultrol ..	0.5	—	Santocure ..	1.25	1.25
Captax ..	—	0.9	DPG .. ..	—	0.3
Santocure ..	0.8	—	Sulphur ..	2	2
Sulphur ..	2.25	2.75			

*Mixing.*—All stocks mixed in "OO" laboratory Banbury using 2-stage mixing technique. In Stage I all ingredients are added except the sulphur and accelerator, which are added an hour later in State II. After overnight cooling the stock is remilled, sheeted and prepared for curing.

*Curing.*—Natural rubber at 275° F. and LTP cures at 290° F., with 5 cures normally prepared to extend from undercure to well into overcure.

In developing the subsequent dual figures for natural rubber and low temperature GR-S the procedure employed in Figure 9 was followed throughout. In every instance the average rubber property values for the eight rubber carbons involved were plotted against the revised specific area values assigned to these carbons in Table I and Figure 8. The plots were drawn as bars with the length representing a reasonable experimental deviation for the particular rubber property. Structure index lines were then developed by simply drawing a smooth curve through those bar plots for carbons of equivalent structure index as shown in Figure 8. Owing to the limited number of carbons involved structure index curves were developed for only the 100, 125 and 200 levels, this range including the extremes and an intermediate level associated with the new fine oil blacks.

### *Mooney Viscosity.*

Viscosity measurements on unvulcanised rubber compounds provide the compounder with the means for assessing probable processing and scorch behaviour. In practice the viscosity limits that can be tolerated are clearly defined. It is of importance then to rationalise the effect of carbon blacks on viscosity, in terms of their dimensional properties as well as the end-use of the compound. It has been recognised for years that there are limits to the levels of fineness and structure in carbon blacks that can be tolerated, determined primarily by their viscosity and scorch

behaviour. These limits are fairly well indicated by the graphical presentation in Figure 10, where Mooney viscosity values are shown for the series of carbons used in this investigation.

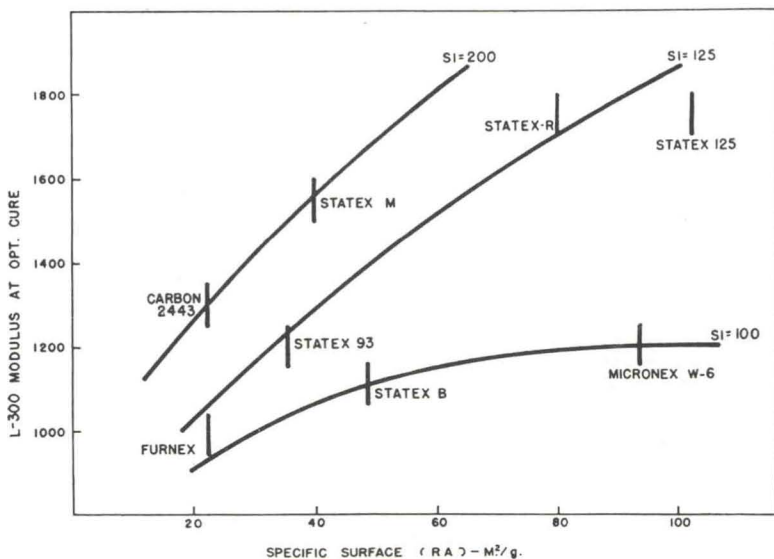


FIG. 9.

Relationship between fineness and structure and Modulus in Hevea for rubber carbons.

It is noted that both structure and surface have a profound effect on Mooney viscosity, with the effect more pronounced in natural rubber than in low temperature GR-S. From the results in Figure 10 the carbon dimension limits currently employed by the rubber industry are indicated as a 200 structure level for carbons below 54 M<sup>2</sup> surface, and a 108 M<sup>2</sup> surface level for carbons in the range of 100-125 structure level. Undoubtedly these limits will be expanded as industry finds means for the practical processing of finer and higher structure carbons.

#### Modulus.

The effects of carbon surface and structure on the L-300 modulus of natural rubber and low temperature GR-S compounds are presented graphically in Figure 11. In every instance the modulus values were taken at optimum cure to equalise as far as possible the cure effect. Optimum cure in our laboratories is based on the tensile curve, selected at a point just short of the maximum.

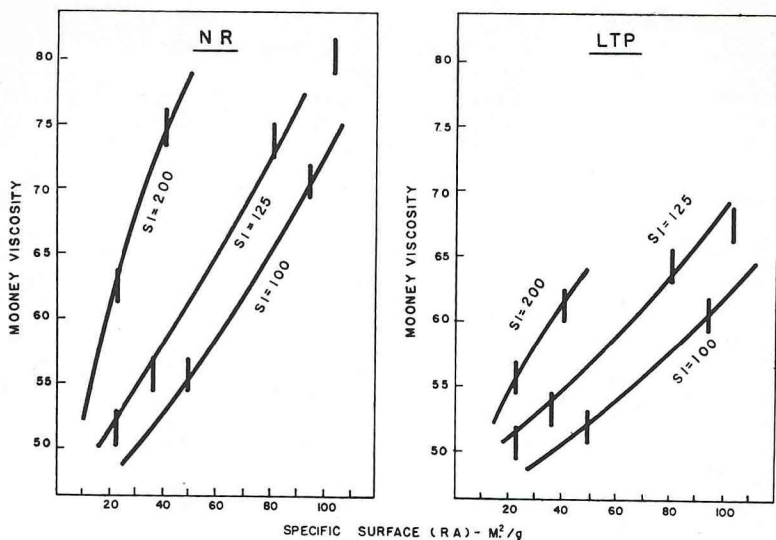


FIG. 10.  
Fineness and structure *and* Mooney viscosity.

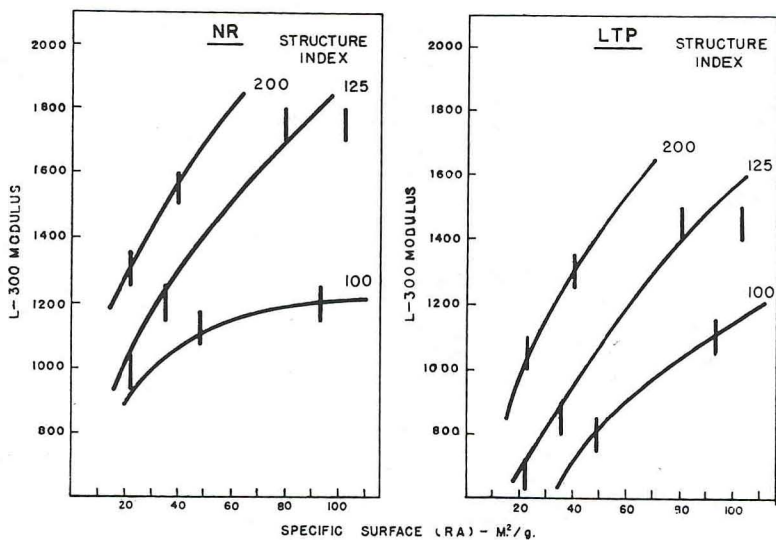


FIG. 11.  
Relationship between fineness and structure *and* modulus.

Fineness and structure are shown to be effective in raising modulus in both polymers with the contribution of surface greater for the high structure carbons. The tendency of the too structure level curve to approach an asymptote, particularly in natural rubber, results from the fact that the only fine carbon in this region is a channel black with a different cure behaviour and a different origin from all the other carbons. The effect of surface in raising modulus is not unexpected in view of the oil absorption—surface trend shown in Figure 6.

Two interesting observations on carbon structure can be mentioned here. If fluffy carbon is used instead of beaded carbon there is a slight dividend in modulus, due probably to the retention of some of the so-called fragile structure. This confirms the oil absorption curve in Figure 5. Secondly, the carbon black separated from a vulcanised compound has been found to have a slightly lower oil absorption value than the original carbon, indicating only a fractional loss during processing of the so-called permanent structure. These observations tend to confirm the usefulness of the oil absorption test as an index to carbon structure persistence in rubber.

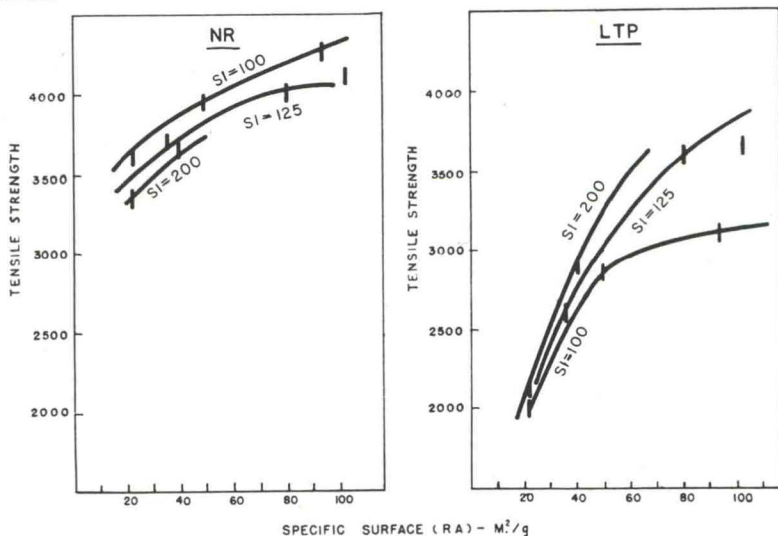


FIG. 12.

Relationship between fineness and structure and tensile strength.

### Tensile.

The surface and structure effects on tensile strength shown in Figure 12 confirm the reported findings of previous investigators, with structure



having a mild depressing effect on natural rubber tensile strength but contributing somewhat to that in the GR-S polymer. It is interesting to note the spreading tendency between the fine furnace blacks and the channel black, most pronounced in the low temperature polymer. Braendle<sup>17</sup> offers a tentative explanation for this reversal effect of structure in the two polymers, based on recognised differences in the crystallising properties of the two polymers.

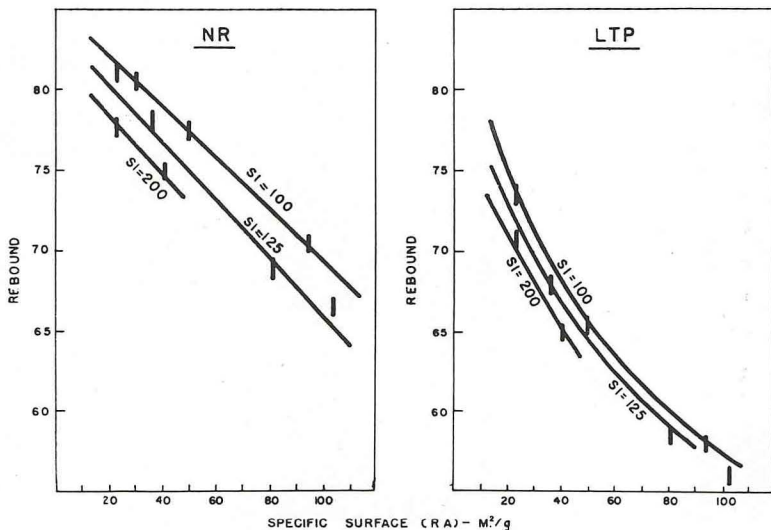


FIG. 13.

Relationship between fineness and structure and rebound.

#### Rebound.

Figure 13 confirms the dominance of surface or fineness on rebound as reported previously by numerous investigators. Structure depresses rebound in both polymers slightly, with the effect somewhat greater in natural rubber. This depressing effect of structure carbons on rebound is ascribed to the actual physical carbon structure introduced into the compound and not to the associated higher modulus. Higher modulus obtained by means other than carbon structure can result in enhanced rather than depressed rebound.

#### Log R.

Electrical resistivity is influenced principally by fineness as shown in Figure 14, with structure playing a secondary but nevertheless significant role as indicated by the results for natural rubber. In the case of low

temperature GR-S the structure effect was not pronounced and could not be graphically shown, due primarily to the low Log R value given for the fine furnace black Statex B. It is recognised that the contact resistance of carbons will vary widely depending on the extent of surface impurities and such differences could well account for this lack of correlation in LTP. Micronex, the only non-furnace carbon in the group, does not fall into the general trend for either polymer due to its high contact resistance resulting from its high combined surface oxygen.

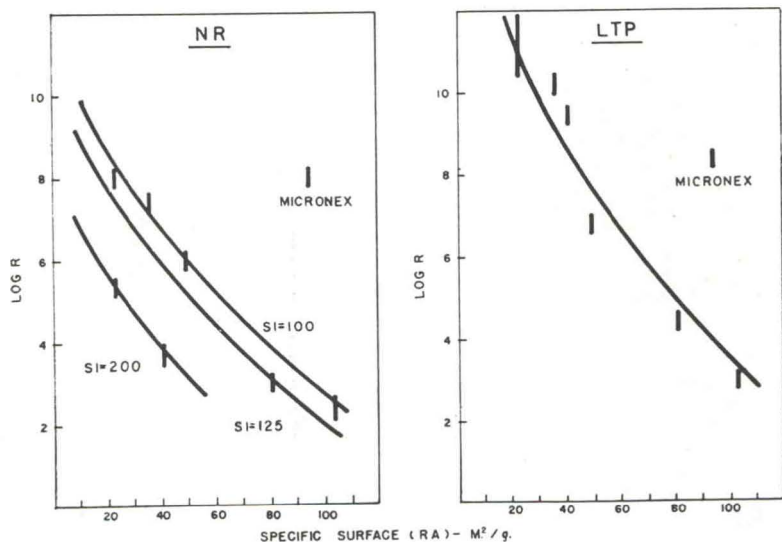


FIG. 14.

Relationship between fineness and structure and log R.

### Extrusion.

One of the most important applications of carbon structure is its use in providing enhanced extrusion properties to rubber compounds. Of primary importance in extrusion applications is the retention of die contour for the extruded stock, with good smoothness and a low swell. In our laboratories fidelity of contour and smoothness is determined by rating the extruded stocks against a set of standards such as shown in Figure 15. A smoothness or surface rating of A with an edge rating of 10 is regarded as the best obtainable.

The extrusion properties in the two polymers for the eight carbons are listed in Table 3, with the edge rating values presented graphically in Figure 16 to demonstrate the role of carbon structure and fineness. The striking effect of carbon structure in improving the extrusion properties

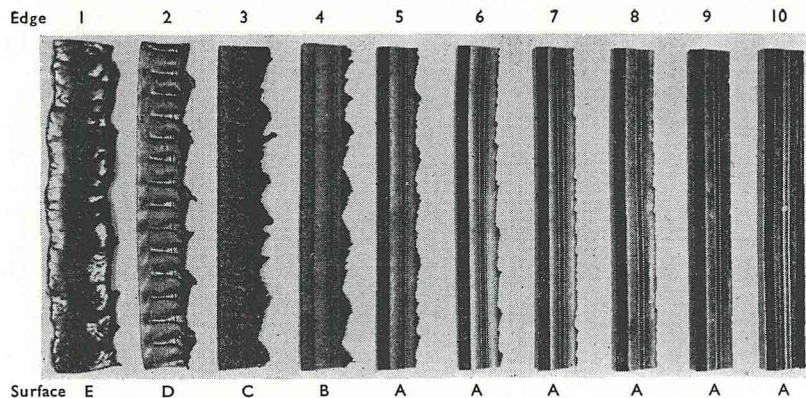


FIG. 15.  
Appearance ratings (garvey die).

TABLE 3  
EXTRUSION PROPERTIES OF RUBBER CARBONS

	2443	Furnex	Statex 93	Statex M	Statex B	Statex R	Statex 125	Micronex W-6
Carbon .. .. .	2443							
In Natural Rubber								
Batch Temp. ° F.	340	335	345	340	340	350	350	350
Mooney viscosity ..	64	52	53	76	51	72	84	71
% Swell .. .. .	30	35	28	24	39	28	39	34
Edge rating .. ..	6	5.5	5.7	6	5.5	6	6.5	5
Surface rating ..	A	A	A	A	A	A	A	A
In LTP								
Batch Temp. ° F.	290	285	290	295	290	300	295	295
Mooney viscosity ..	—	52	53	61	52	64	68	59
% Swell .. .. .	—	114	92	52	122	50	60	111
Edge rating .. ..	7	4	5	9	5	8	6.5	4.5
Surface rating ..	A	B	A	A	B	A	A	B

of LTP compounds is apparent. Particularly effective are the coarser carbons at the 200 structure level, the FEF black for example giving a near perfect result in terms of edge rating and smoothness.

Of interest is the observation that the 100 level structure carbons develop maximum extrusion properties in the surface range of 5 to 6 acres. Also significant is the good extrusion behaviour of the moderate structured fine oil blacks, with the HAF black approaching the effectiveness of the FEF black. The relatively slight effect of either surface or structure on the extrusion properties of natural rubber is ascribed to recognised differences between these two polymers in extrusion behaviour.

#### Abrasion.

Although laboratory abrasion tests are not completely satisfactory indices to road wear performance they do provide indications of potential tyre performance provided comparisons are restricted to a single polymer. Of the various abrasion machines available the Lambourne is regarded in our laboratory as the most satisfactory in predicting road wear. The abrasion data presented graphically in Figure 17 were obtained on the Lambourne, using a slip ratio of 20 for the natural rubber stocks and 24 for the low temperature GR-S stocks.

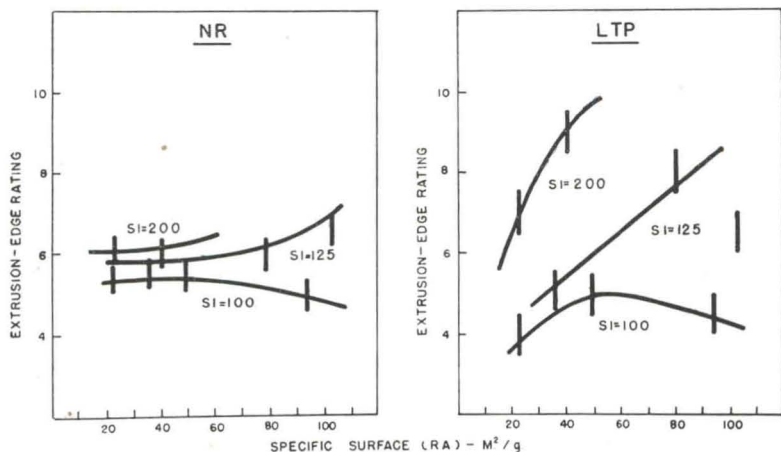


FIG. 16.

Relationship between fineness and structure and extrusion.

It is noted that in both polymers abrasion for the finer carbons is improved markedly by an increase in carbon structure. In the range of coarser carbons the effect of structure is relatively small. Although on



the basis of this graphical record the marked superiority of the moderate structured fine oil blacks over the normal structured channel black is ascribed to a structure differential of 25 units, it seems unlikely that this is the only factor involved in view of the slight additional abrasion advantage shown by the 200 structure level carbons. Other factors, chemical in nature, of which pH may be cited as an example, are undoubtedly involved.

### Road Wear.

It is impossible to develop a valid correlation of fineness and structure with road wear without a sufficiently large number of test results to provide a statistical approach. In the case of Figure 18 the data available, although reliable, were too limited to warrant more than broad band correlations. It is apparent that these trend bands correlate fairly well with Lambourne abrasion, indicating a positive and significant advantage in road wear for carbons of moderate structure in both polymers. In the case of LTP structure contributes appreciably more to road wear than it does in natural rubber. The comments made under abrasion regarding the possible role of factors other than structure and surface would also apply here, to explain the significant divergence between the 100 and 125 structure level bands.

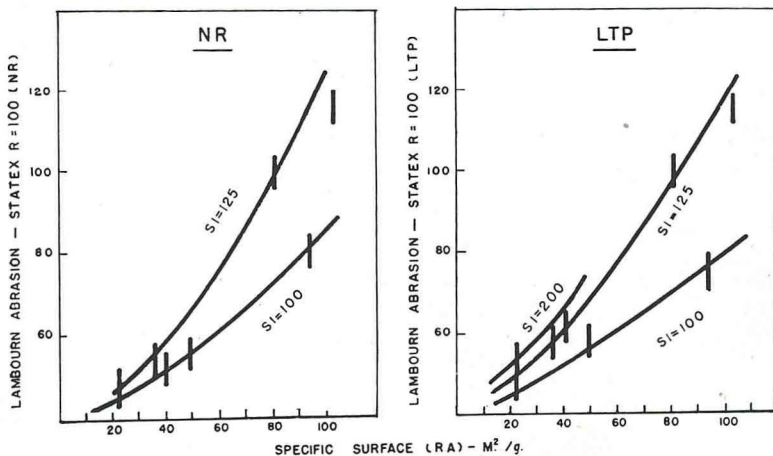


FIG. 17.

Relationship between fineness and structure and lambourne abrasion.

### DISCUSSION

In discussing the stiffening effect of carbon structure in rubber it is realised that other expedients are also available to the rubber compounder for stiffening rubber, although use of such methods does not carry all the

additional advantages associated with the carbon structure effect. Higher loadings, for example, of a lower structure carbon can be used to increase modulus but this approach carries penalties in viscosity, hysteresis, tensile and extrusion performance at equated modulus levels. It is employed only where economies are dictated. Fineness can also be used to provide increased stiffness, as indicated in Figure 10, with significant gains in tensile but a loss in extrusion and a drastic penalty in hysteresis. It is not recommended as a substitute for carbon structure in all those applications where structure is employed, for maximum modulus with minimum hysteresis.

The role of carbon gel in the overall reinforcement picture has received wide attention in recent years and unquestionably must be considered as a contributory factor in the reinforcement phenomenon. Essentially carbon gel involves the development of an insoluble cross-linked carbon-polymer network in the masterbatch stage that sets the pattern for the carbon rubber lattice in the vulcanisate. By selection of the pattern for the carbon or mixing temperature it has been shown<sup>20</sup> that the magnitude of this carbon gel development in the masterbatch stage can be varied significantly, with increases providing higher modulus and hardness levels

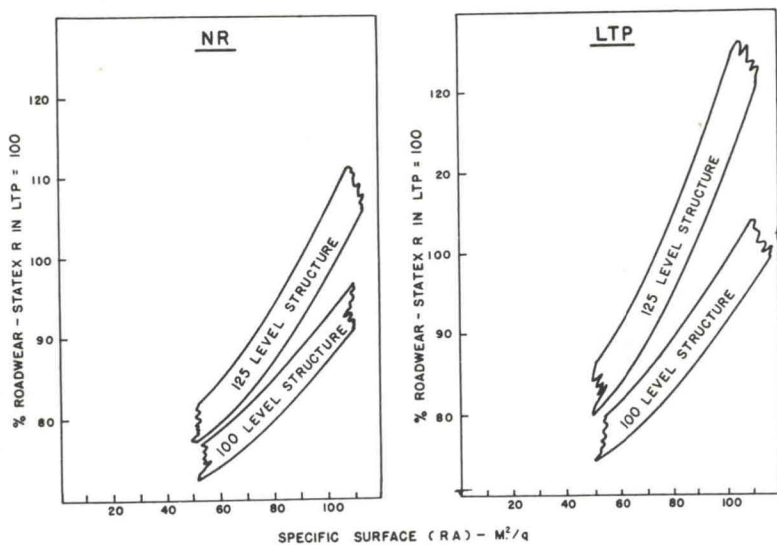


FIG. 18.

Relationship between fineness and structure *and* roadwear.

in the vulcanisate. The role of fineness and structure in this carbon gel development are shown in Figure 19. It is noted that structure raises the carbon gel level significantly in low temperature GR-S but has a negligible effect in natural rubber. This greater activity in LTP suggests

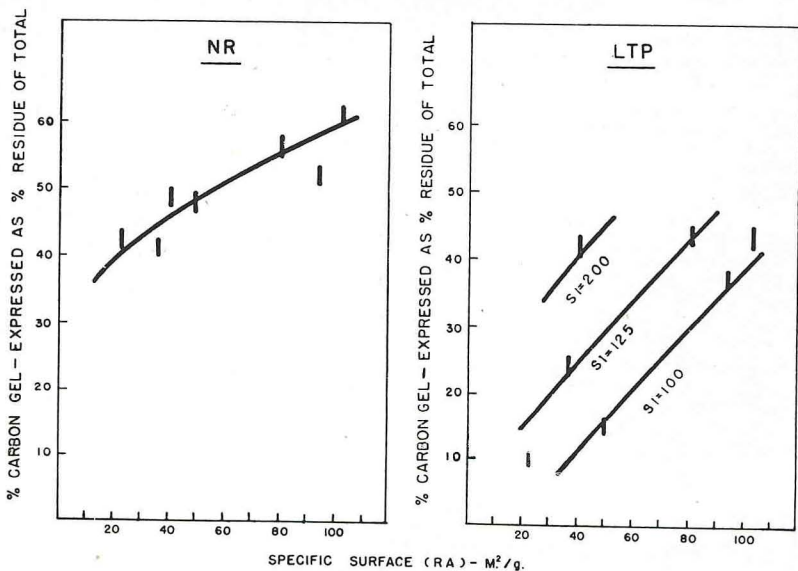


FIG. 19.

Relationship between fineness and structure and carbon gel.

a possible connection of significance between the structure oil blacks and the GR-S type polymer.

The carbon gel approach therefore can also be employed to provide higher modulus with overall effects not too far removed from those associated with carbon structure. But in addition to the added dangers in scorch, due to the higher mixing temperatures required, there are certain deficiencies in extrusion behaviour. In butyl rubber<sup>21</sup> this high temperature approach has been used with success to secure enhanced modulus and abrasion, with the greater stability of this polymer to heat having an important role in this application.

Finally, an amplified cure effect might be employed to raise modulus but the curative adjustments or additional cure times required are so drastic that this method is not considered either practical or economical.

## CONCLUSIONS

Carbon structure is shown to be present in all carbon blacks in varying degree, the persistence of this structure determining its ultimate role in rubber.

The fragile type of structure inherent at the time of manufacture is largely lost in the processing of the dry black, while the more permanent structure largely persists during processing in rubber. This distinction is more one of degree than of kind.

The presence of carbon structure in rubber compounds has been shown to have a significant effect in stiffening rubber. Associated beneficial effects include improved extrusion, abrasion and in the case of tread carbons greater road wear also.

The penalties incurred in obtaining viscosity effects in rubber through carbon structure are mild compared to those encountered when alternative methods are employed.

Carbon structure is the most effective and economical means for securing viscosity and extrusion benefits in rubber with the minimum penalty of hysteresis.

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