

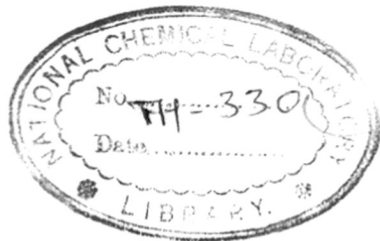
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MOLECULAR STRUCTURE AND ARRANGEMENT
IN ELASTIC PLASTICS WITH PARTICULAR
REFERENCE TO NATURAL AND SYNTHETIC
RUBBER.

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for the
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GENERAL INTRODUCTION.

The present investigation was undertaken as one branch of a broad programme of fundamental research initiated by the Research Association of British Rubber Manufacturers on the relation between the structure and physical properties of rubber-like materials. It was started in 1944 when the rubber industry was faced with a situation of rapidly diminishing stocks of natural rubber, and the problem of the further understanding and development of synthetic products was of foremost importance.

The first part of the work therefore comprised a broad general survey by electron diffraction methods of the existing synthetic rubbers. The materials examined included the butadiene-styrene copolymer used as a general purpose replacement for natural rubber, and a number of the more specialised acrylo-nitrile and polychloroprene materials as well as several thioplasts.

Apart, however, from the simple polychloroprene known in the industry as Neoprene GN, none of these materials showed any signs of orientation on stretching even in the thin films required for electron diffraction, and the information which could be obtained from them by diffraction methods was therefore severely limited. Furthermore,

with the cessation of hostilities in 1945, the immediate urgency of the work on synthetics was relieved. It was consequently decided that the most promising line of research was to concentrate on three representative materials which do show molecular ordering under favourable conditions, and to make a determined effort by means of electron diffraction to gather fundamental information on molecular arrangement. It was hoped that the application of this technique of structure analysis which permits the use of films of a thickness approaching to molecular dimensions, might well lead to an appreciable advance in this direction. This has indeed been found to be the case.

The three materials selected were the two naturally occurring polyisoprenes, rubber and gutta percha, and the synthetic polychloroprene referred to above. All three had already been examined by diffraction methods, particularly by X-rays, but our knowledge concerning their internal structure still remained incomplete and there was thus scope for more detailed study of their structures.

The chief experimental contribution of the work described below lies in the recording of a pattern of diffuse zones in association with the arc pattern obtained by electron diffraction from well oriented specimens of stretched natural rubber. This pattern is similar to

those observed by Charlesby, Finch and Wilman for anthracene and other aromatic compounds (1938, 1939, 1941, 1942) and ascribed by them to thermal vibrations in the material. They recognised that the diffuse zones arose from the individual molecules and not from the lattice as a whole, and that they were particularly valuable in elucidating molecular configuration. The first and principal section of the present work is therefore concerned with the analysis of this background pattern in stretched natural rubber.

The subsidiary section on the examination of natural rubber at low temperatures brings out an interesting phenomenon of orientation of grease on the stretched rubber.

The patterns from gutta percha also show the diffuse patches quite clearly, but these are less readily analysed than in the case of natural rubber as the degree of orientation achieved is less perfect, and the position is further complicated by the polymorphism of the material. The section below on gutta percha is therefore principally concerned with an attempt to analyse the arc and ring patterns obtained under different conditions and to identify them with the appropriate crystalline phases.

In polychloroprene, the only synthetic material

examined here, the pseudo-crystalline diffractions are far less well developed than in either of the two naturally occurring polymers, although the first signs of three dimensional ordering are apparent in some of the patterns. Diffuse bands are also well in evidence in some of the patterns but their origin would appear to be somewhat different. Thus, in the case of natural rubber and gutta percha these bands only occur in association with well developed arc patterns, a circumstance which follows naturally from the theory developed by Charlesby, Finch and Wilman; but here they occur in association with very weak crystalline patterns and it would appear that they are more closely akin to the patterns found for a number of greases, and are indicative of a largely uni-dimensional ordering. This situation is discussed more fully in the section on polychloroprene.

The whole of the work described below was carried out on a Finch-type electron diffraction camera working with a camera-length of 47 cms. and an accelerating voltage of 50-60 kv. This type of camera utilises a cold cathode and a gas discharge chamber. The high voltage current through the system is controlled by means of a diode operated under conditions of saturation and consequently the voltage across the discharge tube is constant, provided the discharge

chamber pressure is constant.

The camera used in the present experiments was evacuated by means of oil diffusion pumps backed by a high speed rotary pump. A 2-stage oil pump was used for the camera body while the discharge chamber was pumped separately by a single stage oil pump. With this system it was possible to maintain a high degree of vacuum in the camera body without interfering with the pressure in the discharge tube. By this arrangement the general background intensity arising from collision of the electron beam with residual gas was kept to a minimum.

THE MOLECULAR STRUCTURE AND ARRANGEMENT IN
STRETCHED NATURAL RUBBER.

1. Introduction.

X-ray fibre diagrams were first obtained from stretched natural rubber by J.R.Katz in 1925. Since then many workers have examined rubber in both the stretched and unstretched state and have made estimates of the lattice constants of the pseudocrystalline structure produced on stretching. C.W.Bunn (1942) recorded an important advance when he arrived at a detailed atomic structure for the extended molecule by appreciating the relative intensity distribution in the X-ray pattern and applying the trial and error method. This structure, though it could not be claimed as final, did not conflict with the observed facts. Other workers, notably Jeffrey, with Cox and Bateman (1942, 1943, 1944) realising that the experimental data available from a fibre diagram are insufficient for a unique Fourier synthesis of the atomic positions, have preferred to examine the crystal structure of relatively simple materials containing isoprene units or related atomic groupings from which the configuration of the elementary units in the poly-isoprene chain might be inferred. It is clear,

however, that we are still far from having reached finality in the determination of the molecular structure and arrangement in natural rubber.

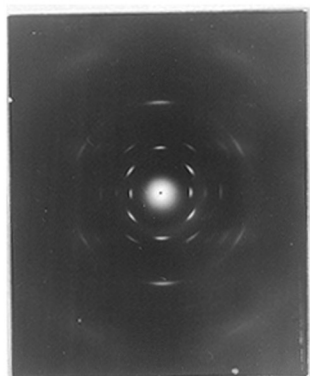
Electron diffraction patterns have been obtained from both stretched and unstretched natural rubber (Trillat and Motz, 1934, Krullov, 1935), but have hitherto added little to the data already provided by X-rays, chiefly owing to the fact that the intensity distribution in the electron diffraction patterns obtained from thin films is so markedly influenced by the relaxation of the third Laue condition.

In 1937 Finch and Wilman first drew attention to the fact that the transmission spot patterns obtained from single crystals of a number of aromatic compounds were associated with a remarkable pattern built up of diffuse areas of scattering, and they recognised that this diffuse scattering pattern originated from the molecule and was not due to the lattice as a whole. Indeed, in 1939, with Charlesby, they showed that this diffuse-zone pattern was due to molecules which, though oriented with respect to the beam in accordance with the crystal orientation, were apparently executing thermal vibrations about their mean lattice positions. The pattern resembled, except for a slowly varying radial factor, that to be expected if the electron beam had been scattered by independent isolated molecules

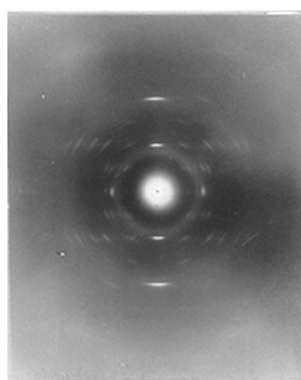
which had the same orientation as in the normal crystal. It is clear that this diffuse background pattern should, on account of its molecular origin, help in determining both the molecular structure and the molecular orientations in organic crystals which exhibit, as in anthracene, sufficient regularity of atomic arrangement within the molecule. It has now been found possible to obtain well-marked diffuse background patterns from stretched raw rubber, and these have thrown fresh light on the structure and arrangement of the molecules in natural rubber.

2. Experimental.

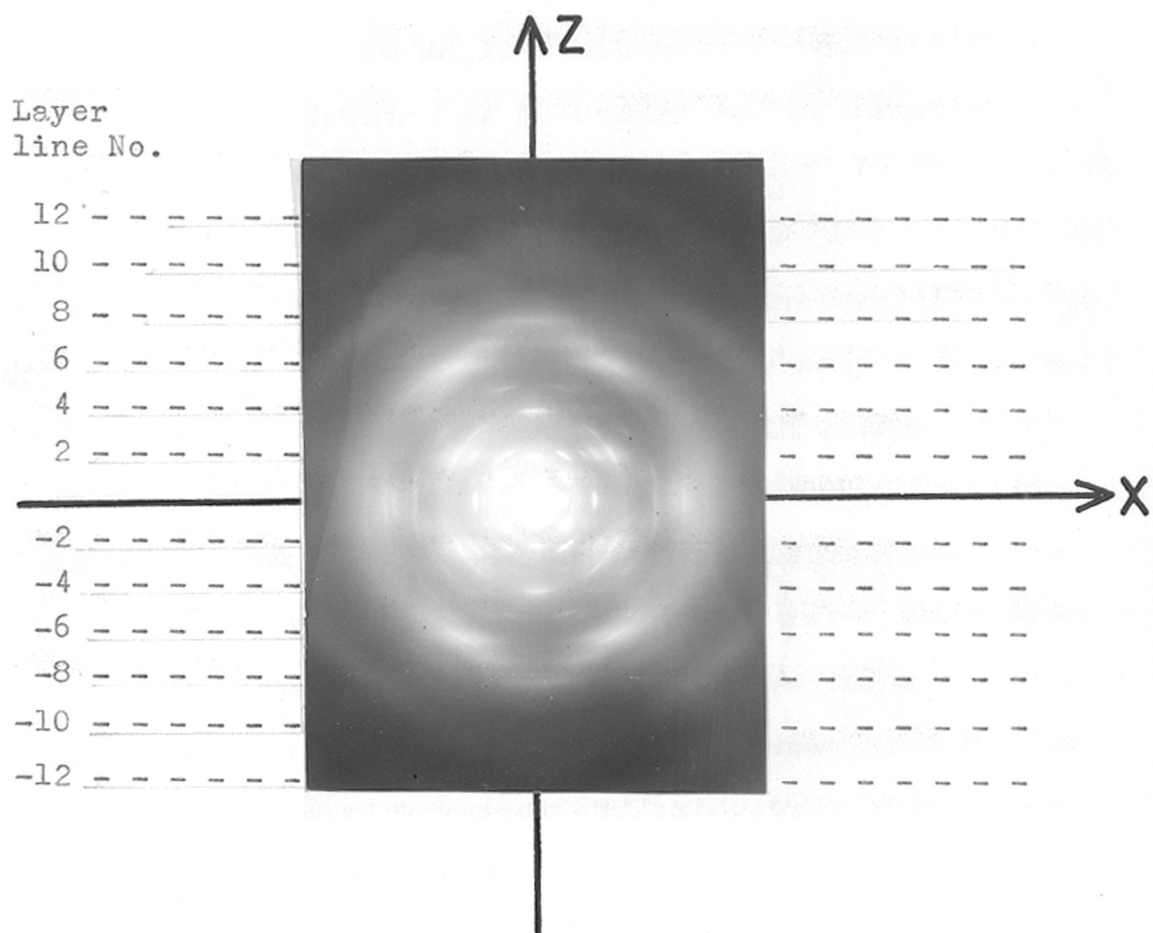
Transmission patterns were obtained from films which were stretched to about ten times their original length, the thickness of the film before stretching being of the order of 2,000 A., as estimated from the interference colours under oblique illumination. The films were prepared by spreading a few drops of a solution of rubber in benzene on a clean water surface in a Langmuir trough; two chromium-plated bars were then placed across the trough and drawn apart, thus stretching the rubber film adhering to their lower surfaces. A portion of the stretched film was then picked up on a grease-free nickel gauze and examined in a Finch-type electron diffraction camera working with a camera



a) Arc pattern with specimen perpendicular to beam. F2244



b) Arc pattern with specimen at 45 to beam. F2246.



c) Pattern showing diffuse zones in addition to arcs. F2794.

Figure 1. Patterns from stretched natural rubber.

length of 47 cm. and an accelerating voltage of 50-60 kv.

The types of pattern obtained are illustrated in figures 1(a), (b), (c). Generally speaking all the patterns showed evidence of both the normal crystalline and the diffuse-zone patterns. The most favourable exposure conditions for bringing out the two were, however, different, a comparatively long exposure being required for the diffuse background pattern. Thus figures 1(a) and (b) show the crystalline patterns obtained with a short exposure (about 10 sec.), with the film perpendicular to the beam for figure 1(a) and inclined at an angle of 45° for figure 1(b), the fibre axis remaining perpendicular to the beam in both cases, while figure 1(c) shows a typical diffuse-zone pattern of long exposure (30 sec.) taken with the film perpendicular to the beam. Well-defined diffuse-zone patterns have not yet been obtained with the film sufficiently inclined to the beam to make any appreciable difference to this pattern, since the greater effective thickness of the film gave rise to sundry confusing effects such as charging-up of the specimen and loss of orientation under the prolonged electron bombardment necessitated by this greater thickness. It is also probable that the diffuse background pattern would still not be given prominently by the steeply inclined films, even if these disturbing influences could be eliminated, because in the

case of a single crystal the intensity of the background pattern relative to that of the spot pattern should, according to Charlesby, Finch and Wilman (1939), vary inversely with the number of atoms in the crystal flooded by the electron beam, which in this case is proportional to the effective thickness of the film.

Absolute values of the spacings in the arc pattern were obtained by direct comparison with the (110) graphite spacing, the graphite being deposited on the rubber specimen in the form of a dilute colloidal suspension in water (Finch and Fordham, 1935; Finch and Wilman, 1937). The value taken for this spacing was 1.228 kx (Nelson and Riley, 1945).

3. The Arc Pattern.

In appreciating the electron diffraction patterns the first step was to ascertain what measure of agreement existed between the arc pattern and the X-ray fibre diagram. A number of unit cells differing in detail have been proposed by various X-ray workers, but as C.W.Bunn (1942) has made the only complete structure analysis, his work was taken as giving the best available data; his proposed unit cell is monoclinic with $a = 12.46$ A., $b = 8.89$ A., c (orientation axis) = 8.10 A., $\beta = 92^\circ$, and space group $P2_1/a$.

It is immediately clear from the difference between

figures 1(a) and 1(b) that the crystalline regions in the rubber films examined here have a strongly preferred orientation in the plane of the rubber film. A rough calculation indicated that this orientation was such that the a and c axes tended to lie in the plane of the rubber film. Working on this basis and using, for a first trial, the orthorhombic cell with a = 12.5 A., b = 8.9 A., c = 8.1 A., $\beta = 90^\circ$, which is a slightly simplified version of Bunn's proposed cell, it was found possible to index all the spots appearing in the present work (Table 1). There were no results specifically requiring the monoclinic cell, but the possibility of this being the true cell cannot be ruled out, as a deviation of 2° in β would not in general be observable in view of the angular spread of the arcs caused by imperfections in the orientation. Bunn himself only introduced this deviation of β from 90° at a late stage in his calculations in order to account for one weak spot which is unlikely to occur in these patterns because the specimen was stationary during the recording of the pattern. The systematic absences, while conforming to the requirements for the space group $P2_1/a$, would equally well satisfy the higher and true orthorhombic symmetry of $P2_12_12_1$ requiring spots of type (h00), (0k0), or (00l) absent for odd values of h, k, or l; but again, reference to Bunn's calculated

intensity values indicates that while (001) spots are theoretically present for odd values of l they are so weak as to be unlikely to appear in the recorded pattern except in unusually favourable circumstances. The intensity distribution among the arcs in the electron diffraction patterns, figures 1(a) and 1(b), cannot be rigorously compared with that of the X-ray pattern, as it is influenced by the extent of the range of orientations present in the specimen, the relaxation of the third Laue condition, and the fact that the specimen was examined in selected stationary positions, thus enhancing the intensity from sets of planes which were preferentially oriented in a direction parallel to the beam. It is nevertheless of interest to note that, making some allowance for these factors, there is good qualitative agreement in intensity distribution between the electron diffraction patterns and the normal (001) oriented X-ray fibre diagram (Table 1). Thus it appears that, while the electron diffraction arc pattern would fit a rather simpler cell having the orthorhombic form and space group $P2_1 2_1 2_1$, there is no evidence which conflicts with the small change in β favoured by Bunn and the space group $P2_1/a$; furthermore, the intensity distribution is in qualitative accord with that of the X-ray patterns.

With regard to the absolute value of the identity period,

Table 1. Comparison of observed spacings with those calculated for orthorhombic cell having $a = 12.5$ A., $b = 8.9$ A., $c = 8.1$ A., and comparison of observed intensities with those found by Bunn.

Indices (hkl)	Electron diffraction patterns				observed	X-ray patterns		
	Spacings		Intensities			observed	Intensities found by Bunn for (001) oriented fibre diagram.	
	Calculated	Observed #	Specimen perpendicular to beam.	Specimen at 45° to beam.			Specimen perpendicular to beam.	Specimen at 45° to beam.
200	6.25	6.21	6.19	VS	-	S	64.5	
120	4.19	4.18	4.14	MW	S	VS	254	
400	3.12	3.08	-	M	-	M	15	
240*}	2.10}	-	-	-	-	-	1	
600 }	2.08 }	-	-	-	-	-	0	
800	1.56	1.54	-	W	-	VVW	4.5	
920	1.33	1.31	-	VW	-	VW	15	
1000	1.25	1.23	-	W	-	VVW	7.5	
111	5.40	-	5.35	-	VW	VW	2	
201	4.95	4.92	4.89	VS	VW	S	24	
121	3.72	-	3.69	VVW	VW	S	27	
311	3.43	3.39	3.37	VVW	VW	MW	5	
401 }	2.92 }	-	-	VVW	-	-	0	
521 }	2.85 }	-	-	-	-	-	-	
231*	2.54	-	-	-	-	MW	3	
611	1.97	-	-	VW	-	-	0.5	
711	1.71	1.70	-	VVW	-	VW	1	
801	1.53	1.51	-	VW	-	VW	1	
002	4.05	4.05	4.05	VS	VS	MW	8	
012*	3.69	-	-	-	-	MW	7	
112	3.54	-	3.51	-	VW	HW	3	
202	3.40	3.40	-	S	-	MS	26	
022*	3.00	-	-	VVW	-	M	6	
122*	2.91	-	-	-	-	-	0.5	
312	2.76	2.75	2.73	VW	W	M	4	

Table 1 (continued).

Indices (hkl)	Electron diffractbn patterns		Intensities observed	
	Spacings		Intensities observed	
	Calculated	Observed #	Specimen perpendicular to beam.	Specimen at 45° to beam.
402	2.47	2.48	-	W
322*	2.43	-	-	W
412}	2.38}	2.38	2.36	VW
132}	2.35}			VW
512	2.07	2.06	2.04	MS
432}	1.90}	-	1.88	-
242}	1.86}			VW
612*	1.81	-	-	VW
113	2.53	-	2.50	-
203	2.48	2.51	-	VVW
123*	2.27	-	-	-
323}	2.02}	2.04	-	VW
403}	2.04}			-
133*	1.97	-	-	-
004	2.02	2.02	2.02	S
124*	1.82	-	-	-
314	1.78	-	1.81	-
205	1.57	1.58	-	VW
506}	1.19}	1.17	-	VW
516}	1.18}			-
008	1.01	1.01	-	VW

* Weak diffractions occurred on photographs from a specimen oriented with its plane at 60° to the beam.

† Values given here are rough means of hkl and $\bar{h}k\bar{l}$ values

S = strong; M = medium; W = weak; V = very.

X-ray patterns.

Intensities found by Bunn for (001) oriented fibre diagram.

Observed	Calculated †
VVW	1
MW	2 } 7 } 0.5 }
M	6
M	2 }
	0 }
VVW	2
MW	11 }
	1 }
MW	6
MW	3
MW	1
MW	9
MW	6 }
	0 }

No layer lines higher than 4th order mentioned.

These spacings are calculated relative to rubber (001) = 8.1A. for comparison with the trial cell. Absolute values are discussed elsewhere.

however, a real discrepancy between the electron diffraction results and Bunn's values appears. Thus the best estimates of a and c measured against the graphite standard (110) ring, 1.228 kx. (Nelson and Riley, 1945), were 12.46 ± 0.02 kx. and 8.23 ± 0.02 kx., compared with Bunn's values of 12.46 A. and 8.10 A. respectively, from which it is seen that the present estimate of the identity period differs significantly from Bunn's value of 8.10 A., although the two values for the a axis are in good agreement. These measurements were made on strong arcs of the (h00) and (00l) type and the graphite comparison ring was introduced by permitting a drop of diluted graphite suspension in water to spread out on the stretched rubber film. The third axial length b was not investigated in detail as no spots of the (0k0) type appear in transmission patterns on account of the strongly preferred orientation with this axis perpendicular to the plane of the rubber film.

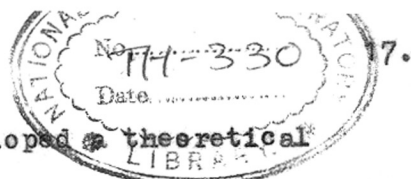
Notwithstanding the difference in the absolute value of the identity period, the general agreement in form between the electron diffraction and X-ray results justifies the use of Bunn's atomic co-ordinates as a basis for a preliminary investigation of the molecular origin of the diffuse-zone pattern.

4. The Diffuse-Zone Pattern.

The pattern reproduced in figure 1(c) shows three distinct features: these are (i) the haloes characteristic of the amorphous or liquid state, (ii) a pattern of arcs forming a typical crystal fibre diagram, and finally, (iii) a number of diffuse zones, the so-called diffuse background pattern ascribed by Charlesby, Finch and Wilman (1939, 1941, 1942) to molecular displacement by thermal motions. It is in these zones and their relation to the crystalline pattern that the main interest of this work lies.

Since the diffuse zones in the inner regions of the pattern are associated with clusters of arcs it might at first be thought that they arise from some distortion of the crystalline lattice giving rise to broadening of the arcs. Two considerations, however, indicate that this cannot be the whole explanation of the diffuse-zone pattern; these are that the broadening does not increase with increasing angle of diffraction, and that the diffuse zones occur in the outer regions of the pattern where there is no sign of associated arcs. Consequently we are led to some further consideration of the observed pattern in relation to the characteristics which would be expected in the molecular thermal vibration theory.

In connection with their work on anthracene, Charlesby,



Finch and Wilman (1937, 1939) developed a theoretical expression for the intensity arising from a group of rigid molecules oriented in accordance with the crystalline arrangement, but undergoing thermal vibrations. They found that the resulting pattern should consist of two parts: (i) the Laue spot pattern characteristic of the periodicities of the crystal lattice, and (ii) a pattern of diffuse zones characteristic of the atomic arrangement within the molecules, and that the intensities of the diffuse zones should increase relatively to those of the Laue spots with increasing angle of diffraction. These conclusions were borne out by their diffraction patterns from anthracene, and the present rubber patterns show closely similar features, for it has been shown that the arc pattern corresponds to the normal crystalline arrangement, and it is readily apparent from figure 1(c) that the diffuse zones become increasingly more intense relative to the arcs with increasing angle of diffraction, in fact, they remain prominent in the outer regions of the recorded pattern where the arcs have ceased to be even faintly visible.

Thus the evidence points strongly towards the conclusion that the observed diffuse-zone pattern has this molecular origin. In what follows it is assumed that this is the case and consequently that the arrangement of the

diffuse zones is characteristic of the atomic arrangement within the molecules and should therefore enable us to define the structure of rubber more closely than has hitherto been possible.

In order to use the diffuse-zone pattern in this way it is first necessary to consider the general form of the molecules involved and to make certain broad assumptions as to the manner in which they may be expected to vibrate. It is generally accepted that natural rubber is a long chain polymer of isoprene, C_5H_8 , and that its rubber-like properties arise from the great flexibility which the molecules exhibit on account of the freedom of rotation of consecutive units about single bond linkages. It is therefore obvious that the theory developed for anthracene, in which the molecules were treated as rigid vibrating entities cannot be applied directly to the long flexible molecules of rubber; a fundamental treatment of the problem requires some account to be taken of the relative movements of the atoms within the molecule. As a beginning, however, the simplified case can be examined where the molecule is regarded as being divided into fairly short segments which undergo displacements relative to one another as a result of thermal vibrations while the atoms within a segment remain at rest relative to one another.

The question then arises as to what length of the

molecule can be considered to be included in a single segment. One obvious choice would be to regard each isoprene unit as a virtually rigid vibrating entity. There would, however, be some considerable simplification in the work of interpreting the diffuse-zone pattern if it were supposed to arise from a longer length of the molecule, since such a segment, including a number of identical units, would show a greater degree of geometrical regularity. It therefore seems worth considering whether any such choice would be reasonable, and in this connection it is necessary to consider the arrangement of the molecules in an extended specimen of rubber. The stretched material is believed to contain a number of pseudocrystalline regions where sections of the chain molecules, oriented parallel to one another by the stretching, have linked together to form a three dimensional array; these regions are interspersed with disordered regions where the molecules are twisted and tangled in an entirely random manner. The length of a single molecular chain is about 10,000 A. (Staudinger and Bondy, 1930), while the average linear extent of a crystalline region, as indicated by the breadth of the arcs in the X-ray fibre diagram, has been estimated to be of the order of 600 A. (Hengstenberg and Mark, 1928). Thus a single chain is likely to pass through several regions of order and disorder. The effect on the fibre diagram of increasing the extension is to enhance its

intensity relative to that of the halo pattern without in any way altering the crystalline spacings; thus it would appear that further extension causes more of the material to take up the ordered arrangement while leaving those regions which were already crystalline unaffected. On the other hand, the disordered regions are never entirely smoothed out however great the extension, as is apparent from the persistence of the halo pattern right up to the maximum extension which the material will maintain without fracture.

It would thus appear that we can legitimately regard the extended rubber specimen as comprising large numbers of comparatively rigid crystalline regions interlaced with disordered regions of greater mobility on which the continued extensibility of the material depends. From this argument it is apparent that there is some justification for supposing that the part of any chain molecule included in a single crystalline region might, to a first approximation, undergo thermal vibrations as a rigid unit. Such a segment would have a definite repeat unit in the direction of the orientation axis (the identity period of the arc pattern), and could only give rise to diffractions along the same lines as the arcs in the crystal pattern. Reference to the pattern, figure 1(c), shows that, except for a small angular spread similar to that observed in the arc pattern, the zones do in

fact lie near these same lines, thus giving experimental support to the hypothesis. Therefore, in the discussion which follows, the diffuse-zone pattern has been treated as though it arose from molecular segments containing at least 10 to 15 repeat units and with a total length of some 100 A., each behaving as a self-contained array of scattering centres diffracting quite independently of any adjacent chain or any other segment in the same chain. It is nevertheless appreciated that once the general lay-out of the molecule has been defined some further refinements may be obtained by taking into account the relative movements of atom groups within a segment and considering the pattern to be anticipated from individual isoprene units. An investigation of this kind is now being undertaken.

The interpretation of the pattern has been approached by the trial and error method, and in order to do so it was first necessary to make some deductions, based on reasoning from other evidence, as to the atomic structure of the molecule. As mentioned above, rubber is a long chain polymer of isoprene, C_5H_8 ; the identity period along the extended chain is such that it must include two isoprene units, and Bunn (1942) has shown conclusively that it takes up the cis form in relation to the double bonds. By analogy with the long chain hydrocarbons it might be anticipated

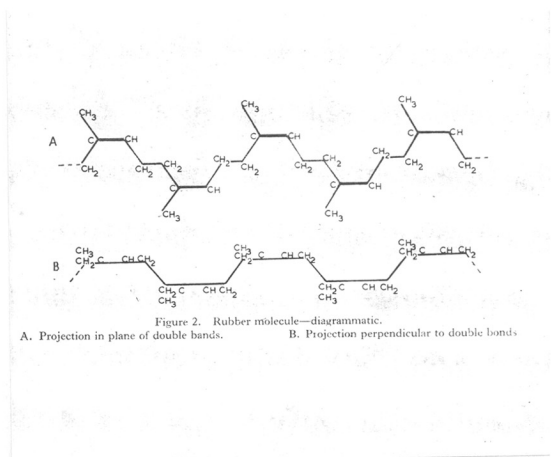
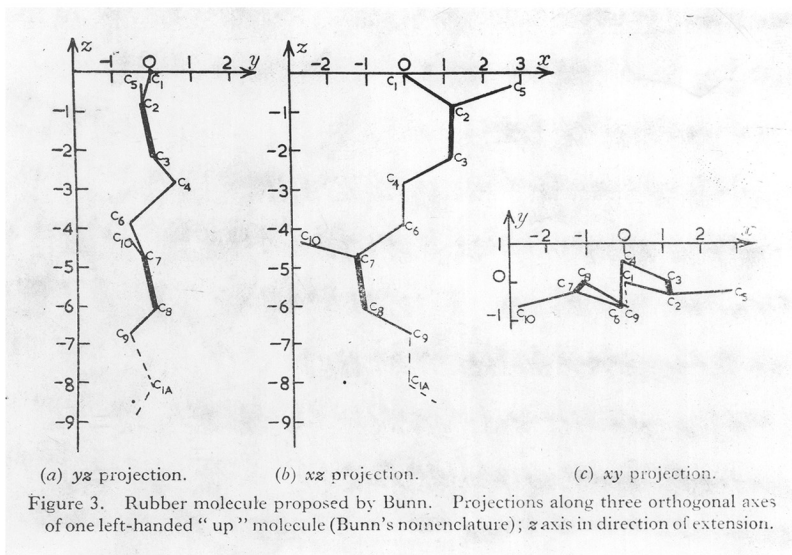


Figure 2. Rubber molecule—diagrammatic.
 A. Projection in plane of double bands. B. Projection perpendicular to double bands.

Figure 2.

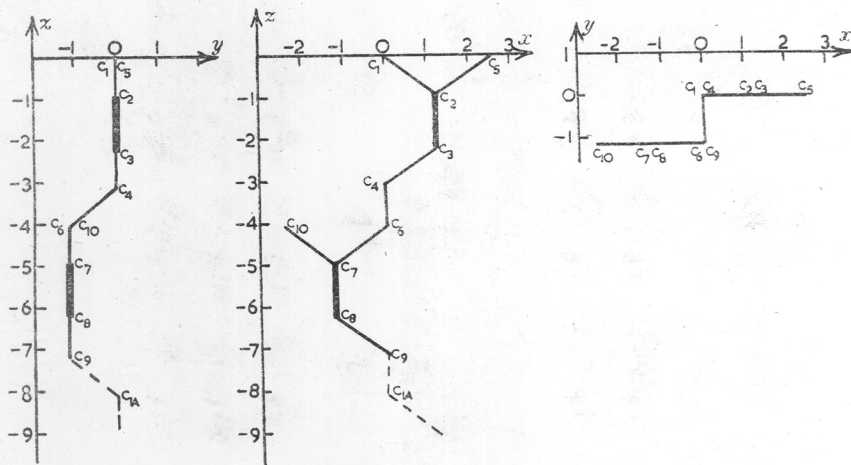
Rubber Molecule - Diagrammatic

that the chain would be planar, but the identity period along the axis of elongation, which all observers agree to be in the region of 8.1 - 8.2 Å., is too short to permit this without serious and improbable distortions of the accepted bond lengths and angles; consequently we are forced to the conclusion that the molecule is non-planar. There are, then, many ways in which the chain can be supposed to be kinked and twisted to give the observed identity period. For the present work, however, two models have been selected for investigation: the first is the structure proposed by Bunn which was taken because it was the only complete structure so far proposed on the basis of direct experimental results; the second, hypothetical, structure has been chosen as involving the minimum of distortion from the wholly planar form, and therefore forming a useful basic model on which further modifications can be imposed if necessary. It is a model in which all the carbon atoms of each isoprene unit are planar and the planes of consecutive units are parallel to each other and to the orientation axis; furthermore, all bond lengths and angles are normal, the reduction in identity period being attained by straining the connecting links between consecutive units out of the plane, so that the molecule forms a series of steps up and down as indicated diagrammatically in figure 2.



This was, in fact, the molecule selected by Bunn as the initial basis for his calculations, but in order to satisfy his X-ray spot intensities he subsequently modified it considerably by introducing certain distortions in the bond lengths and angles and moving the methyl group out of the main plane of the isoprene unit. The atomic co-ordinates for one complete repeat unit of each structure are shown in Tables 2 and 3, and their projections along three rectangular axes in figures 3 and 4.

The problem then is to find the positions of the intensity maxima arising from a chain segment comprising ten to fifteen such units. In computing such a pattern we have to take into account two factors: the form of the individual unit, and the existence of a number of such units along the segment forming effectively a line diffraction grating with a definite identity period. It is only at those positions where both conditions are favourable that maxima can occur. The line grating alone would give rise to maxima along regularly spaced lines perpendicular to its own length, while the individual unit would give a more complex two-dimensional pattern. Consequently, in the computations which follow, the method adopted has been to select the lines along which the identity period permits maxima to occur and to examine the intensity variations which the atomic arrangement in the single unit gives rise to



(a) yz projection.

(b) xz projection.

(c) xy projection.

Figure 4. Suggested rubber molecule with planar isoprene units and standard bond lengths and angles. Projections along three orthogonal axes: z axis in direction of extension.

Table 2. Atomic co-ordinates (A), for Bunn's molecule. Single repeat unit

(a) As given by Bunn, Proc. Roy. Soc. A, 1942, 180, 56. Left handed "up" molecule. Referred to crystallographic axes $a = 12.46$, $b = 8.89$, $c = 8.10$ A., $\alpha = \gamma = 90^\circ$, $\beta = 92^\circ$.

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
	(CH ₂)	(C)	(CH)	(CH ₂)	(CH ₃)	(CH ₂)	(C)	(CH)	(CH ₂)	(CH ₃)
x ₁	0.753a	0.854a	0.845a	0.745a	0.968a	0.744a	0.644a	0.659a	0.757a	0.532a
y ₁	0.899b	0.865b	0.905b	0.959b	0.876b	0.834b	0.874b	0.905b	0.834b	0.828b
z ₁	0.802c	0.703c	0.542c	0.457c	0.773c	0.326c	0.215c	0.052c	0.025c	0.268c

(b) Referred to three orthogonal axes x, y, z and to C₁ as origin. y and z are parallel to b and c respectively.

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
x	0.000	1.259	1.147	-0.100	2.680	-0.112	-1.357	-1.172	0.050	-2.755
y	0.000	-0.303	0.052	0.533	-0.205	-0.577	-0.222	0.053	-0.577	-0.632
z	0.000	-0.846	-2.145	-2.792	-0.328	-3.851	-4.703	-6.034	-6.702	-4.224

Table 3. Atomic co-ordinates (A), for simple molecule having plane units and standard bond lengths and angles - Single repeat unit.

(a) Referred to orthogonal axes x, y, z, and to C₄ as origin.

	C ₁ (CH ₂)	C ₂ (C)	C ₃ (CH)	C ₄ (CH ₂)	C ₅ (CH ₂)	C ₆ (CH ₂)	C ₇ (C)	C ₈ (CH)	C ₉ (CH ₂)	C ₁₀ (CH ₂)
x	0	1.26	1.26	0	2.51	0.04	-1.22	-1.22	0.04	-2.48
y	0	0	0	0	0	-1.22	-1.22	-1.22	-1.22	-1.22
z	0	-0.89	-2.22	-3.11	0	-4.05	-4.94	-6.27	-7.16	-4.05

(b) Referred to axes x, y, z as above, and to the midpoint of C₄ - C₆ as origin.

	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀
x	-0.02	1.24	1.24	-0.02	2.49	0.02	-1.24	-1.24	0.02	-2.50
y	0.61	0.61	0.61	0.61	0.61	-0.61	-0.61	-0.61	-0.61	-0.61
z	3.58	2.69	1.36	0.47	3.58	-0.47	-1.36	-2.69	-3.58	-0.47

along these lines. In other words, the calculations are made as for a single unit, but the repetition of this unit along the molecular segment introduces a geometrical regularity which limits the regions over which the resulting pattern need be considered.

Since the molecular segment is non-planar, it is no longer possible to construct a single two-dimensional intensity contour map adaptable to any crystal orientation by simple linear transformation of the axial lengths as was done in the case of anthracene; instead, each orientation requires a separate contour diagram. However, the only diffuse-zone patterns considered in this work were taken with the plane of the rubber film effectively perpendicular to the electron beam, and the arc patterns, figures 1(a) and 1(b), indicate a strongly preferred orientation with the ac crystallographic plane lying in this plane. Consequently we are principally concerned with this one orientation for which the x and z axes of atomic co-ordinates (which are in the ac plane), figures 3 and 4, are perpendicular to the electron beam and the y axis is parallel to it. In computing the anticipated intensity distribution for this orientation it is only necessary, as will be shown below, to take into account the x and z atomic co-ordinates of the molecule. More generally, for other orientations, the diffraction pattern can be considered as practically that

which would be obtained from the projection of the molecule in the plane perpendicular to the electron beam.

The (010) orientation in the film plane is not quite perfect; thus the appearance of certain spots of the general (hkl) type in the pattern taken with the film perpendicular to the beam (Table 1) indicates a partial rotation about the c axis. In addition, the c axis itself shows some angular deviation from its mean position within the ac plane as is indicated by the drawing out of all spots into arcs of about 10° angular range, and it seems likely that it will similarly suffer some angular deviation in the plane perpendicular to this. The most probable situation is something approaching a Gaussian distribution of orientation with its maximum frequency in the (010) orientation, and such a state of affairs would be expected to result in some broadening of the intensity maxima, but should not give rise to any peaks not anticipated for the preferred orientation. If the angular spread of direction of the b axis is similar to that exhibited by the c axis in the (010) plane the broadening will not be appreciable since an angular deviation of $\pm 5^\circ$ about an axis normal to the electron beam produces little change in the projection of the molecule normal to the beam. In what follows, therefore, the pattern has been computed for the single orientation with the xz plane normal to the electron beam.

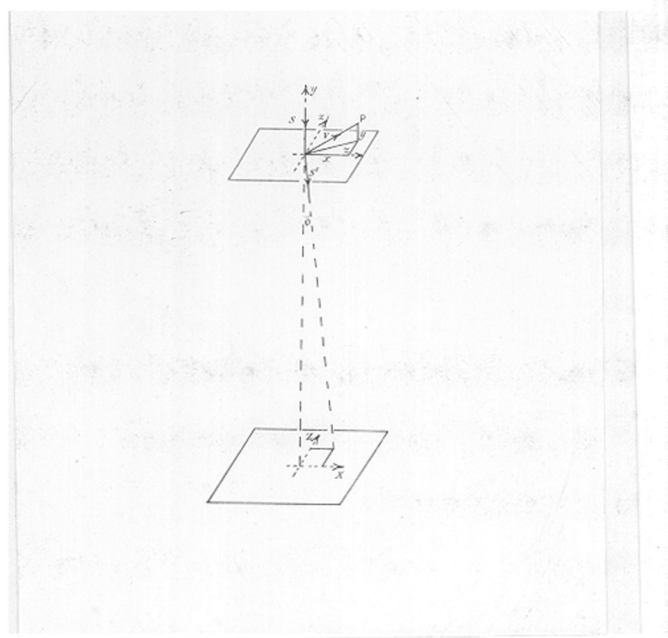


Figure 5

Illustration for derivation of
intensity relationship

The calculation of intensities is based on the following argument (see Figure 5):-

Suppose the amplitude of the wave diffracted by any atom p in the direction \underline{s}' from a wave incident in a direction \underline{s} to be E_p (where \underline{s} and \underline{s}' are unit vectors). The intensity of the wave resulting from a group of such atoms is obtained by adding the amplitudes of the constituent diffracted waves, having due regard to their phases, and squaring the result.

Thus the resultant intensity is given by the expression

$$\left\{ \sum_p E_p \cos(2\pi d_p / \lambda) \right\}^2 + \left\{ \sum_p E_p \sin(2\pi d_p / \lambda) \right\}^2$$

where d_p is the path difference between the wavelet scattered from p and from an arbitrary origin, and λ is the wavelength of the radiation considered.

For an atom whose position relative to the origin is given by the vector \underline{r}_p we have

$$\begin{aligned} d_p &= \underline{r}_p \cdot (\underline{s}' - \underline{s}) \\ &= (\underline{x}_p + \underline{y}_p + \underline{z}_p) \cdot (\underline{s}' - \underline{s}) \\ &= (\underline{x}_p + \underline{z}_p) \cdot (\underline{s}' - \underline{s}) \text{ since } \underline{y}_p \cdot (\underline{s}' - \underline{s}) \approx 0 \end{aligned}$$

for small ϕ .

If the directions \underline{s}' and \underline{s} strike the photographic plate in points X , Z and O , O referred to axes in the plate we have

$$\underline{s}' = \frac{(\underline{X} + \underline{Z} + \underline{L})}{\sqrt{X^2 + Z^2 + L^2}} \text{ where } L \text{ is the camera length}$$

$$(\underline{X} + \underline{Z} + \underline{L})L \text{ since } \phi \leq 2^\circ$$

and $\underline{S} = \underline{L}/L$
 so that $(\underline{S}' - \underline{S}) = (\underline{X} + \underline{Z})/L$

Hence, the expression for the intensity becomes

$$\left\{ \sum_P E_p \cos[2\pi/\lambda (\underline{x}_p + \underline{z}_p) \cdot (\underline{X} + \underline{Z})/L] \right\}^2 + \left\{ \sum_P E_p \sin[2\pi/\lambda (\underline{x}_p + \underline{z}_p) \cdot (\underline{X} + \underline{Z})/L] \right\}^2 \\
= \left\{ \sum_P E_p \cos[2\pi/\lambda L (\underline{x}_p X + \underline{z}_p Z)] \right\}^2 + \left\{ \sum_P E_p \sin[2\pi/\lambda L (\underline{x}_p X + \underline{z}_p Z)] \right\}^2 \quad (1)$$

where \underline{X} and \underline{Z} are taken parallel respectively to \underline{x} and \underline{z} , and the axes are rectangular.

The amplitude E_p of the wave diffracted from an individual atom depends on the scattering power of the atom and on the angle of scattering, the latter relationship resulting in a falling off of intensity from the centre towards the outer parts of the pattern. With regard to the scattering power of the atoms concerned, the hydrogen atoms have been neglected as separate scattering centres, but have been regarded as adding a little to the effective weight of the carbon atom to which they are attached; thus the scattering factors of the C, CH, CH₂ and CH₃ groups have been taken in the ratio 6:7:8:9, which assumption was also made by Bunn in determining his atomic co-ordinates.

In computing intensities the following standard conditions have been taken: the factor λL has been taken as 2.75 A.cm. (for direct comparison with an experimental pattern the dimensions of the computed pattern have been

reduced in the ratio $L(\text{observed})/2.75$, and the origin of co-ordinates has been taken as coinciding with the carbon atom C_1 (Figures 3 and 4). Atomic co-ordinates have been measured in Angstrom units, and co-ordinates on the photographic plate in centimetres.

Thus, substituting for the various known or assumed values, the expression used in the computations of intensity at any point X, Z of the photographic plate becomes, for the Bunn molecule,

$$\left\{ \begin{array}{l} 8 \cos \\ +6 \cos \\ +7 \cos \\ +8 \cos \\ +9 \cos \\ +8 \cos \\ +6 \cos \\ +7 \cos \\ +8 \cos \\ +9 \cos \end{array} \right\} \left[\begin{array}{l} (360/2.75) \\ 360/2.75 \\ (360/2.75) \\ (360/2.75) \\ 360/2.75 \\ (360/2.75) \\ (360/2.75) \\ (360/2.75) \\ (360/2.75) \\ (360/2.75) \end{array} \right] \left\{ \begin{array}{l} 0 \quad - \quad 0 \\ 1.259X \quad - \quad 0.846Z \\ 1.147X \quad - \quad 2.145Z \\ -0.100X \quad - \quad 2.792Z \\ 2.680X \quad - \quad 0.328Z \\ -0.112X \quad - \quad 3.851Z \\ -1.357X \quad - \quad 4.703Z \\ -1.172X \quad - \quad 6.034Z \\ 0.050X \quad - \quad 6.702Z \\ -2.755X \quad - \quad 4.224Z \end{array} \right\}^2$$

$$+ \left\{ \begin{array}{l} 8 \sin \\ +6 \sin \\ +7 \sin \\ +8 \sin \\ +9 \sin \\ +8 \sin \\ +6 \sin \\ +7 \sin \\ +8 \sin \\ +9 \sin \end{array} \right\} \left[\begin{array}{l} (360/2.75) \\ (360/2.75) \\ (360/2.75) \\ (360/2.75) \\ (360/2.75) \\ (360/2.75) \\ (360/2.75) \\ (360/2.75) \\ (360/2.75) \\ (360/2.75) \end{array} \right] \left\{ \begin{array}{l} 0 \quad - \quad 0 \\ 1.259X \quad - \quad 0.846Z \\ 1.147X \quad - \quad 2.145Z \\ -0.100X \quad - \quad 2.792Z \\ 2.680X \quad - \quad 0.328Z \\ -0.112X \quad - \quad 3.851Z \\ -1.357X \quad - \quad 4.703Z \\ -1.172X \quad - \quad 6.034Z \\ 0.050X \quad - \quad 6.702Z \\ -2.755X \quad - \quad 4.224Z \end{array} \right\}^2 \quad (2)$$

and for the second, less distorted, molecule, a similar expression holds but with the appropriate atomic co-ordinates substituted for the Bunn co-ordinates.

With an identity period of 8.1 A. and with $\lambda L = 2.75$ the "layer-line" separation is $2.75/8.1$ cm.; in other words the lines near which our preliminary assumptions permit intensity maxima to occur have Z values (taken to the nearest $\frac{1}{2}$ mm.) of 0, 0.35, 0.7, 1.05, 1.35, 1.7, 2.05, 2.4, 2.75 etc. cm. Inspection of the photographs, however, suggests that the most pronounced maxima lie on the even-order layer lines (as might be expected from the similarity in form of the two halves of the molecule) and consequently the computations have been confined to those lines. They were carried out in general at 2 mm. intervals along these lines except in a few cases where intermediate values were obtained. Angles in the structure-factor expression were taken to the nearest degree.

The molecule has four possible orientations in the film, for the conditions governing its orientation are that the c axis direction (z axis of co-ordinates) shall lie in the direction of extension, and that the plane of the isoprene units (xz projection) shall be parallel to the plane of the film. From Figures 3(a) and 4(a), which show the appropriate projection, these conditions are seen still to be fulfilled if the whole molecule is rotated through 180° about the x or z axis or both. Taking the axes of co-ordinates as fixed in relation to the film this is equivalent to changing the

sign of either the x or z co-ordinates, or both. Now it is reasonable to suppose that any section of the film impinged on by the electron beam will include equal numbers of molecules in all the possible orientations; consequently in computing it is necessary to consider the intensities arising from each of these orientations, the resulting intensity at any point being the sum of that due to the separate constituents taking into account the basic assumption of no phase relationship between adjacent molecules. In fact it is only necessary to consider two of the orientations because, owing to the squares, the expression (1) for the intensity arising from a single molecular unit is not affected when the signs of both the atomic co-ordinates are reversed. It is also only necessary to consider one quadrant of the pattern because the effect on the expression (1) of reversing the sign of either X or Z is precisely the same as that of reversing the sign of the corresponding atomic co-ordinates. In the case of the undistorted molecule the atomic configuration shows some degree of symmetry which is best seen from Table 2(b) in which the origin of co-ordinates has been moved to the midpoint of the repeat unit. This introduces a further simplification to the computations, for the two orientations x, z and x, -z now give identical intensity distributions as long as we confine ourselves to

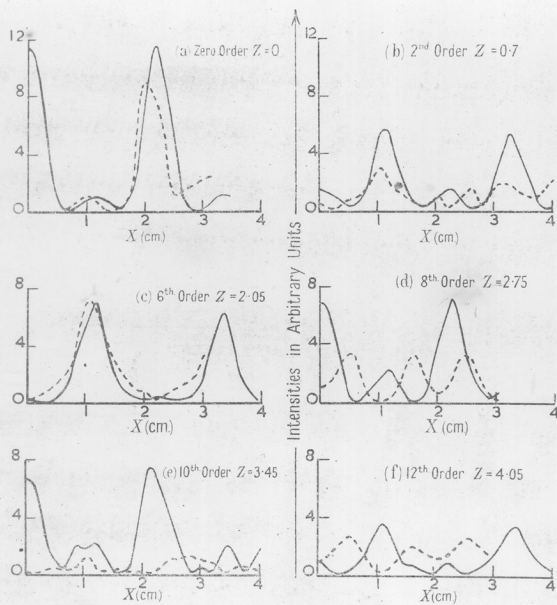


Figure 6. Computed intensities along layer lines for the two atomic configurations investigated.

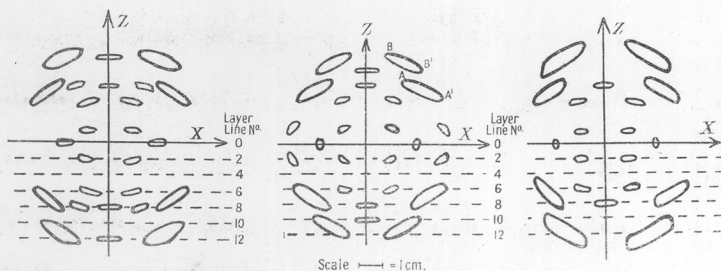
———— Model with planar units and standard bond lengths and angles.

----- Model due to C. W. Bunn.

the layer lines; for, provided that the ten atoms of the repeat unit are regarded as repeating indefinitely (which is what confining our attention to the layer lines implies), a change from the x, z to the $x, -z$ orientation merely implies a change of origin from the point C_1 to the point C_6 (Table 3), which cannot have any effect on the computed pattern since the choice of origin is purely arbitrary. Therefore for the undistorted model calculations were carried out for the x, z orientation only, and the values were multiplied by two to compare with the assumed intensities for the two orientations of the Bunn molecule.

5. Comparison of Computed Patterns with Observed Pattern.

The computed intensity distributions along the zero, 2nd, 6th, 8th, 10th and 12th layer lines are shown in Figures 6(a)-(f). The fourth layer line has been omitted as it showed no pronounced maxima. An attempt has been made to construct the patterns which would be anticipated from the positions of these maxima, and the results are shown in Figures 7(a) and 7(b), together with a trace taken from an experimental pattern, figure 7(c). In constructing these patterns it has been assumed that the visible breadth of the diffraction maxima corresponds to the half-maximum breadth of the intensity peak, and that the imperfections of



(a) Computed pattern for model due to Bunn.

(b) Computed pattern for model with planar units and standard bond lengths and angles.

(c) Observed pattern (traced from figure 1 (c)).

Figure 7. Computed and observed diffuse zone patterns.

molecular orientation are of the order indicated by the extent of the arcs in the Laue spot pattern, so that the whole pattern suffers an angular spread of about 9° . The length of the molecular segment considered has been taken as sufficient to limit the layer lines to true lines, the apparent breadth of the diffuse zones in the c axis direction arising solely from the small rotation referred to above.

The similarity in form between the computed and experimental patterns is readily apparent and gives ample support to the fundamental theory on which the calculations are based; that is, we are justified in assuming that the observed diffuse-zone pattern arises from molecules which are oriented much as in the crystal but behave as entirely independent groups of scattering centres. In other words, the pattern is characteristic of what would be expected from a group of oriented molecules in a pseudo-gaseous phase.

A close inspection of the curves (Figures 6(a)-(f)) reveals significant differences between the intensity distributions from the two models. The most striking difference is along the eighth layer line where the two curves of Figure 6(d) show entirely different characteristics, the Bunn model giving rise to three weak peaks at roughly 0.5, 1.5 and 2.5 cm. from the centre, while the undistorted model gives a strong central peak, and a second of about the

same intensity at 2.2 cm. Comparison with Figure 1(c) and with the traced experimental pattern, Figure 7(c), shows that the undistorted model is in far better agreement with experiment in this region; in fact, along this line the agreement is exact within the technical limitations of the patterns. The next characteristic difference between the two models is that the undistorted form gives sharper peaks; thus on the tenth and twelfth layer lines the Bunn model shows no pronounced peaks, but only certain wide zones of slightly increased intensity, while the undistorted model and the experimental pattern both show well defined peaks along these lines. The experimental data and undistorted model pattern are again in fairly good agreement in relation to peaks at 2.2 and 1.1 cm. on the tenth and twelfth orders respectively; these could well coalesce and give rise to the extended zone BB' (Figure 7(b)), though the position of this observed zone is not quite what would be expected from the computed intensities. The error is probably not serious since the observed pattern is very faint and of poor definition in these outer regions, and the computed intensity maxima here are highly sensitive to small changes in the atomic co-ordinates owing to the large values of their coefficients. Along the zero and sixth order layer lines the two computed patterns are in good agreement with one another and with observation. On the second order line they

differ again slightly, the undistorted model still giving more definite peaks though, while the peak at 1 cm. accords well with observation, the moderate peak to be expected at 3.2 cm. is absent from the experimental pattern.

It would thus appear that while both the molecular models investigated give rise to patterns agreeing in their broad general characteristics with those actually observed in the diffuse-zone electron-diffraction pattern, a more detailed examination shows that the computed intensity curves from the undistorted model are in much closer agreement with the facts than is the case with Bunn's model. This agreement is in fact remarkably good, the only discrepancy being the absence from the experimental pattern of a peak to be expected, in the case of the undistorted model, on the second order layer line at 3.2 cm. In particular, the undistorted model gives much the better agreement along the eighth order layer line, where the most sharply defined zones in the experimental pattern occur, and where Bunn's model gives an intensity distribution which is entirely at variance with observation.

6. Conclusions.

Although there are still some minor discrepancies to be resolved, the appearance of the diffuse-zone electron-diffraction pattern arising from thin films of stretched

natural rubber is adequately explained on the basis of the thermal oscillations of the long-chain rubber molecules in the crystalline regions, this pattern being analogous with that which would be given by a stream of oriented molecules in a pseudo-gaseous condition. As Charlesby, Finch and Wilman (1939) pointed out the diffuse-zone pattern has distinct advantages in the examination of complex molecules, since it gives a direct indication of the configuration of the molecule independent of its mode of fitting into any particular crystalline lattice. In spite of the diffuseness of the patterns with which we are dealing a study of the diffuse zone or molecular pattern has shown that it is possible to discriminate decisively between two postulated atomic configurations which do not differ greatly.

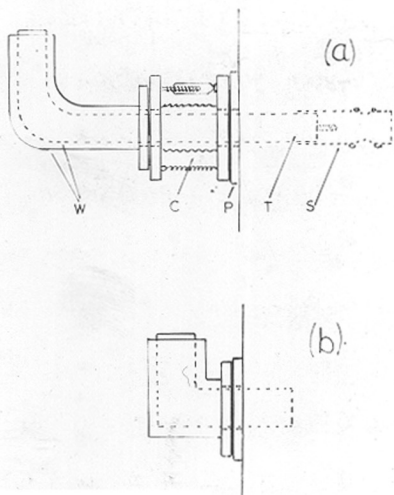
In the case of natural rubber, neither of the two configurations investigated agrees in every respect with experiment, but the evidence brought forward above supports the view that the atomic arrangement in the stretched rubber molecule approximates to a simple form having planar units and standard bond lengths and angles, rather than to the more complex form hitherto considered.

LOW TEMPERATURE PATTERNS AND ORIENTATION OF
GREASES ON STRETCHED NATURAL RUBBER.

1. Introduction.

A series of experiments were carried out in which the rubber film was cooled down with liquid air during its exposure to the electron beam, with the object of ascertaining what effect a reduction in temperature would have on the diffuse zone pattern. In the course of these experiments it was noticed that certain of the low temperature patterns included a number of arcs which could not be fitted into the normal rubber pattern, but which on measurement conformed to the spacings of the normal long chain hydrocarbons. The traces of hydrocarbon were due, no doubt, to the condensation of oil pump vapours. It was soon evident that the hydrocarbon crystallites had taken up an orientation related to that of the rubber molecule.

This interesting phenomenon was followed up because it was hoped that the epitaxial behaviour of the hydrocarbon deposit might in itself afford a pointer to the rubber film structure.



- C Standard carrier with 'tombac' flexible metal tubing, adjusting screws, etc.
- P Camera port.
- T Tube containing liquid air.
- W Double walls to tube T, space between being evacuated.
- S Shield to protect specimen from condensation of residual vapours.

Figure 8.

- (a) Low temperature specimen carrier.
- (b) Auxiliary liquid air container.

2. Experimental.

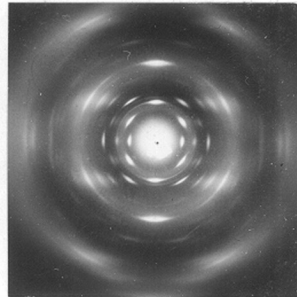
Stretched rubber specimens were prepared and mounted on nickel gauze as for the room temperature experiments, but for the low temperature work the specimens were mounted in a special specimen holder of a type previously developed and used in this laboratory for low temperature work, and later used by Charlesby (1945). This holder is shown diagrammatically in Figure 8a. It utilises the standard carrier providing universal motion of the specimen by means of "tombac" flexible metal tubing and adjusting screws, but differs from the standard holder in that the central shaft which carries the specimen comprises a hollow metal tube closed at the end to which the specimen is attached and open at the other end. During an experiment this tube is filled with liquid air or other convenient liquid, thus cooling the specimen through the metal end of the tube. For convenience the outer portion of the tube is bent upwards, and in order to minimise the heat exchanges with the atmosphere this outer portion is provided with double walls, the space between them being open to the camera. In these particular experiments in which the transmission method of diffraction was used, the specimen gauze was supported on a solid metal ring which was firmly screwed to the end of the liquid air tube so as to ensure good heat conduction to the specimen.

Finally the specimen was enclosed by a tubular metallic shield which fitted over the end of the tube. This served the double purpose of ensuring that the specimen was completely surrounded by cooled metal (apart from the holes necessarily provided in the shield for the passage of the electron beam) and of protecting the specimen to some extent from the condensation of adventitious impurities such as water vapour and hydrocarbons.

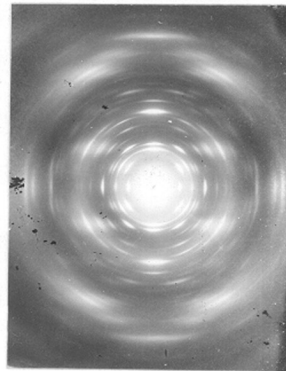
In spite of this precaution, however, condensation of impurities still occurred and in some experiments a second liquid air container was inserted at one of the spare camera ports; this was cooled down well in advance of the specimen holder and so collected most of the impurities before the specimen was cooled. This container, shown diagrammatically in Figure 8b was similar in principle to the specimen holder but since its only function was to provide a cold surface inside the camera, no adjustment in its position was necessary and the flexible jointing etc was dispensed with and the tube fitted directly to the camera by means of the standard greased joint.

For the room temperature experiments on deposition of the normal hydrocarbons on rubber three materials were tried - paraffin wax, white vaseline, and liquid paraffin. White vaseline was found to be the most convenient, because the boiling point of paraffin wax was rather too high, whilst

a) Specimen at low temperature
for 5 minutes. F2652



b) Specimen at low temperature
for 15 minutes.
Shows oriented grease
pattern in addition to normal
rubber pattern. F2655



c) Graphite comparison pattern
after 15 minutes at low
temperature. F2744

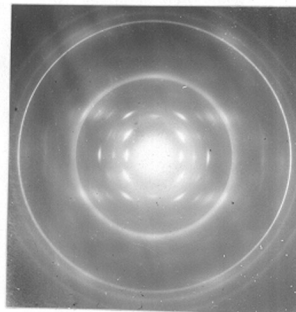


Figure 9.

Low temperature patterns from stretched natural rubber.

the liquid paraffin tended to evaporate in the electron beam. The experiments reported below were therefore all made with white vaseline.

The grease was deposited on the rubber specimen either at atmospheric pressure or in a molecular beam in the evacuated diffraction camera. The former method was extremely simple and was found to be quite effective, though care had to be taken to avoid appreciable heating of the rubber film. Deposition of the grease as a molecular stream in the camera was also easily effected and enabled the grease film to be built up layer by layer.

3. Experimental Results.

a). Low temperature patterns.

The patterns obtained are illustrated in Figure 9a, b, and c. Figure 9a shows the pattern obtained five minutes after the holder had been filled with liquid air, and Figure 9b the pattern observed ten minutes later, the holder being kept filled with liquid air during the intervening period. Figure 9c is a graphite comparison pattern obtained after fifteen minutes.

The pattern of Figure 9a is seen to be very similar to that obtained at room temperature, although measurement of the a/c axial ratio indicates that this is slightly reduced, the value now being 1.50₅ against 1.51₄ for the

room temperature patterns; in other words, the molecular chains have become rather more closely packed. The exposure to the electron beam was not sufficiently extended to bring up the diffuse zones strongly in the outer regions of the plate but they can be quite clearly seen in Figure 9a in the region covered by the arc pattern, and in the original negative they can also be detected in the outer parts.

In Figure 9b the brightness of both the arcs and the diffuse zones appears to be enhanced and the axial ratio is still further reduced, being now only 1.48_3 . The most remarkable feature of this pattern, however, is that it shows a number of extra spots, and since many of these fall in positions intermediate between the layer lines of the rubber pattern they are not due to the normal rubber structure. It is, of course, not surprising that a foreign material should appear in these patterns since most experimenters working at these low temperatures have found that stray vapours tend to condense on the specimen, but it is remarkable that these additional arcs show that the material from which they originated had a high degree of orientation closely associated with that of the stretched rubber film. This additional pattern has therefore been investigated further with the following results.

The strongest arcs in this auxiliary pattern are those

which occur along the orientation axis of the rubber and just outside the rubber (002) and (004) arcs respectively. Assuming that the rubber retains its room-temperature identity period of 8.23 kx. along the c axis these correspond to spacings of 3.60 and 1.80 kx respectively. The next most characteristic feature is the faint ring which passes almost through the rubber (120) and (002) arcs and has more intense regions on it at approximately 60° to the orientation axis of the rubber. This corresponds to a spacing of 4.06 kx and the arcs lie on a line perpendicular to the fibre axis (c) of the rubber and halfway between the centre of the pattern and the 3.60 arc, thus suggesting the possibility that the auxiliary pattern may arise from a rectangular cross grating with one axis of length 7.20 kx in the direction of the rubber orientation axis. This view was confirmed by the finding of six arcs which could all be fitted to a rectangular lattice of axial lengths 7.20 kx. and 5.0 kx. These spacings are set out in Table 4. The values 7.20 and 5.0 suggest that the material may be one of the long chain hydrocarbons and the experimental conditions make this highly probable since the camera atmosphere is known to contain some vapour from the high-vacuum greases and oils used in the pumping equipment. As further confirmation a plate referring to the 32-carbon atom material $C_{32}H_{66}$ was remeasured and the

spacings are set out in Table 4. The similarity between the two is obvious, the only real difference being in the appearance in the latter of the (001) spacing at 2.58 kx. which could, of course, not occur in the pattern from hydrocarbon films viewed in the chain direction. It therefore seems reasonable to conclude that the auxiliary pattern arises from one of the long chain paraffins which is in [001] orientation with the chains perpendicular to the substrate, and also shows very strong azimuthal orientation in the ab plane closely correlated with the axial directions in the ac plane of the rubber.

Table 4.

<u>'Grease arcs' in low temp. pattern</u>			<u>C₃₂H₆₆</u>		
(Spacings in terms of rubber <u>c</u> axis = 8.23 kx.)			(Spacings (A) determined from camera length and sphere gap voltage)		
Observed spacings kx.	hkl	Calc. spacing for a = 7.20 kx, b = 5.00 kx.	Observed spacings A	hkl	Calc. spacings for a = 7.40 A, b = 4.96 A
(Absolute values from rubber standard).					
4.06	110	4.11	4.12	110	4.12
3.60	200	3.60	3.70	200	3.70
2.92	210	2.92	2.97	210	2.97
			2.58	001	-
2.46	020	2.50	2.48	020	2.48
				300	2.47
2.17	310	2.16	2.21	310	2.21
1.80	400	1.80	2.06	320	2.06

(Spacing in Angstrom Units = 1.002 x Spacing in kx. Units)

Figure 9c shows a graphite comparison pattern obtained after the specimen had been maintained at the low temperature for one hour. The lattice constants of graphite do not appear to have been examined at temperatures below 0°C., and there is consequently some uncertainty in the value of its (110) spacing in the present experiments. Nelson and Piley (1945) have, however, investigated the thermal expansion of graphite by X-ray methods over the temperature range 14.6°C. - 800°C., and found that the length of the a axis does not vary by more than 0.00056 kx. over the whole of this range. It is therefore unlikely that any error is involved in taking the room temperature value of 1.228 kx. as a true standard in the present experiments where axial lengths are quoted only to two decimal places.

The value thus obtained for the c axis in the cooled rubber is 8.27 kx. This figure is rather higher than the room temperature value of 8.23 ± 0.02 kx., but the difference is unlikely to be significant since the low temperature value was obtained from one pattern only. Morss (1938), who examined stretched rubber by X-ray diffraction at 20°C. and -120°C. also found that there was no change in the length of the c axis though the a/c ratio changed from 1.52 at room temperature to 1.48 at -120°C.

It is of interest to note that although this graphite

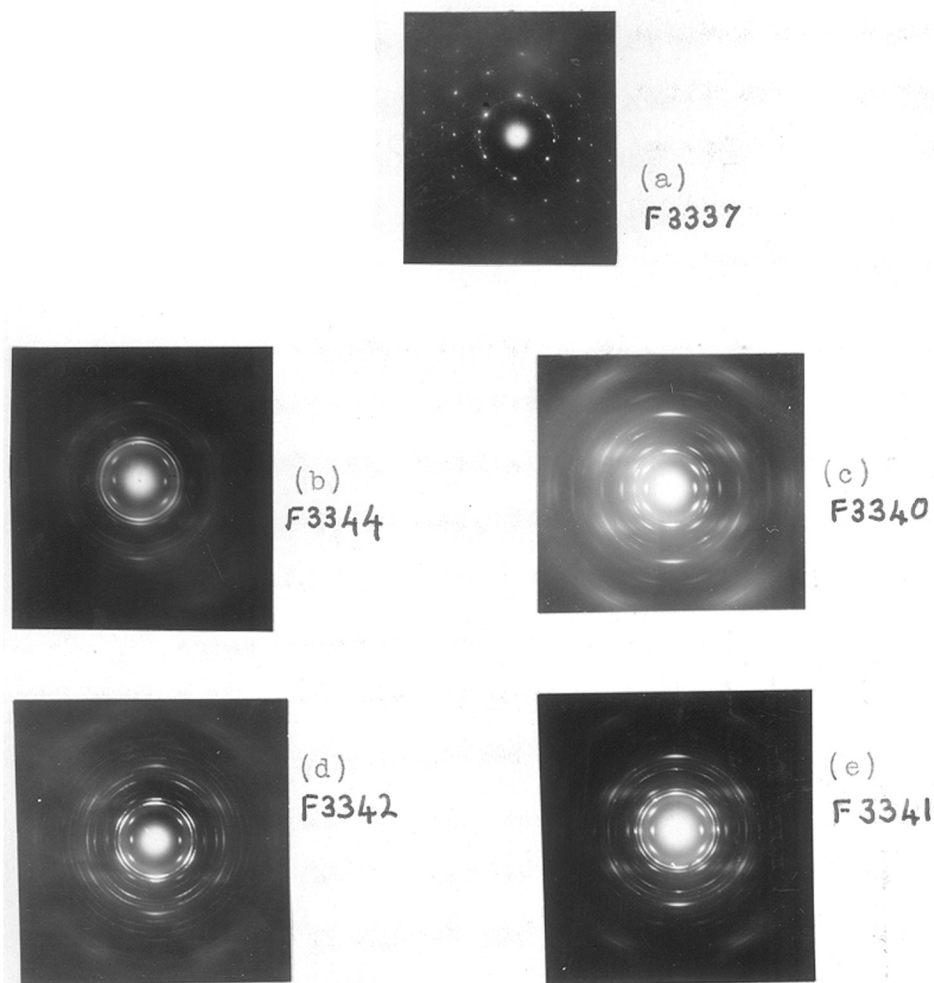


Figure 10.

Patterns from vaseline evaporated on to stretched rubber.

(a), Vaseline alone from part of specimen from which rubber was missing. Almost single crystal pattern.

(b) to (e), Various combinations of orientations of vaseline on the stretched rubber.

comparison specimen was maintained at the low temperature for an hour, there is no trace of the normal hydrocarbon pattern in Figure 9c. It appears that the graphite film not only prevents the orientation of the grease crystallites on the rubber but also inhibits their formation.

b). Room Temperature Patterns from Vaseline Evaporated onto Rubber.

Several of these patterns are illustrated in Figure 10. Figures 10 a, c, d, and e were obtained from specimens in which the vaseline was deposited at atmospheric pressure and Figure 10b from one where it was deposited in the form of a molecular vapour stream inside the camera. White vaseline is a mixture of normal hydrocarbons with chain lengths in the region of 20-35 carbon atoms, and Figure 10a given by a part of the specimen where the rubber film was apparently absent, is a characteristic normal hydrocarbon pattern. It is practically a single crystal pattern from a hydrocarbon crystal orientated with its long chain axis in the direction of the electron beam. It shows clearly the network on which the more complex patterns from the normal hydrocarbons are based. Figures 10 b-e all show the spacings of both natural rubber and the normal hydrocarbons.

The observed hydrocarbon spacings are given in Table 5. They are all of the (hk0) type which indicates that these

molecules are oriented with their long chain direction parallel to the electron beam. That is to say, since the films were examined perpendicular to the electron beam, the long chain direction of the hydrocarbon molecules is perpendicular to the rubber film on which they are deposited. Furthermore, the vaseline patterns all show strong azimuthal orientation associated with the direction of the rubber fibre (c) axis as indicated by the fact that they are symmetrical with respect to this axis.

Table 5.

Spacings from Vaseline condensed on to Stretched Rubber at Room Temperature.

(Spacings relative to rubber (001) = 8.23 kx.)

Observed Spacings kx.	Indices (hkl)	Spacings Computed for a = 7.41 kx b = 4.96 kx.
4.12	110	4.12
3.71	200	3.70
2.48	020	2.48
2.22	310	2.21
2.06	220	2.06
1.24	040	1.24

This azimuthal orientation will now be considered in more detail. The projections in the film plane of the crystal lattice of rubber (a c projection), and the normal

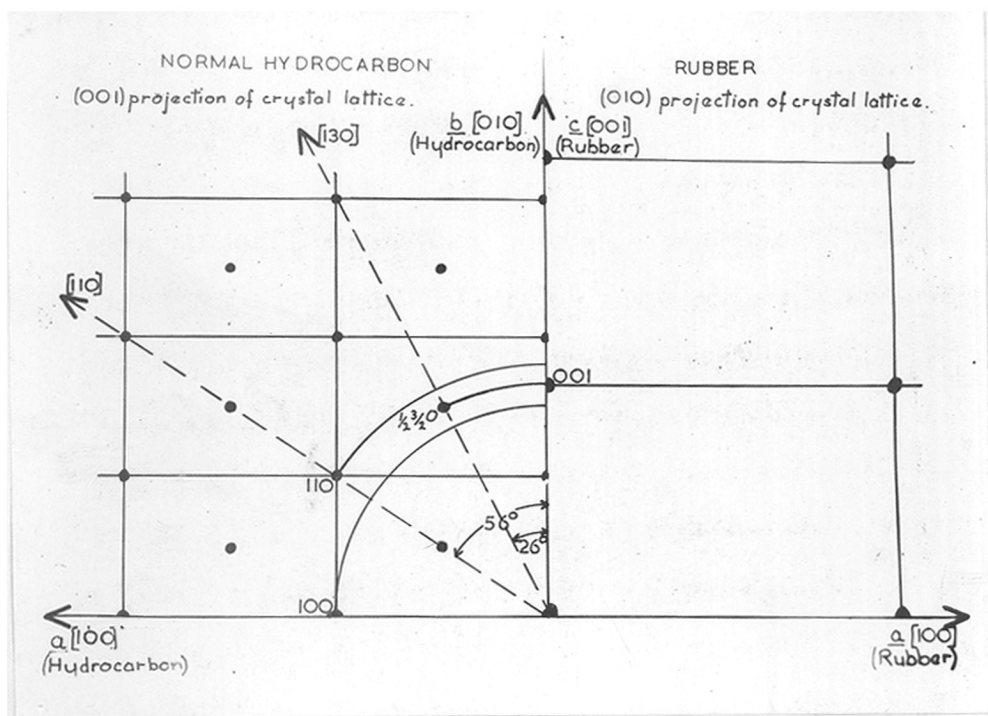


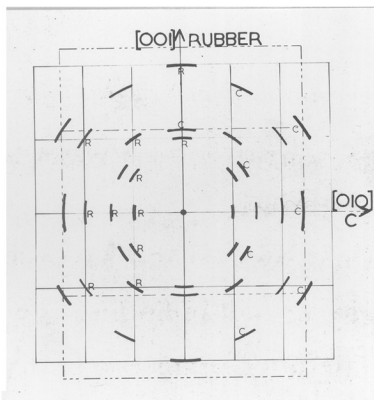
Figure 11a.

Crystal lattices of normal hydrocarbons (white vaseline) and stretched natural rubber.

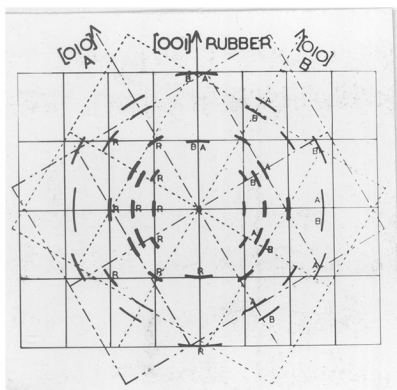
Note similarity of marked spacings along atom rows in the hydrocarbon lattice to that along the 001 atom row in the rubber.

hydrocarbon (a b projection), are shown in Figure 11a. It will be seen from this figure that there are three types of atom row in the normal hydrocarbon which have atomic spacings close to the identity period of the rubber in the direction of its c axis (8.23 kx.). These are the [100], [$\frac{1}{2}$ $\frac{3}{2}$ 0] and [110] atom rows with atomic spacings of 7.41 kx, 8.31 kx, and 8.92 kx respectively, which differ by 10%, 1%, and 8% from the rubber spacing of 8.23 kx.

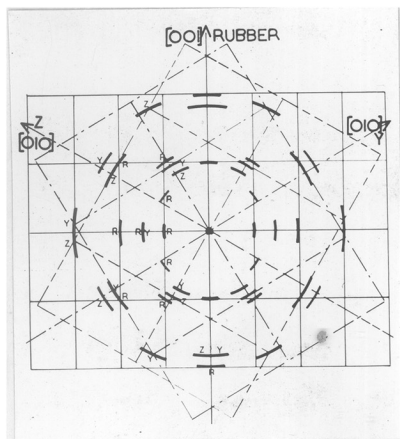
Crystal growth of long chain organic compounds on similar molecular organic substrates does not appear to have been studied hitherto although Willems (1938, 1940, 1943) has observed oriented overgrowths of organic crystals on inorganic substrates. In general, however, epitaxial behaviour is encouraged by similarity of spacings along interfacial atom rows in substrate and deposit. When, as in the present case, the deposited crystals are formed by condensation from vapour, there appears to be considerable tolerance in the lattice constants, in fact parallel growth has been found to occur when lattice constants of the substrate and deposit differed by as much as 50% (Royer, 1928, 1933, 1934, 1935; Finch and Whitmore, 1938; Whitmore, 1939; Goche and Wilman, 1939; Wilman, 1940, etc.etc.). The orientation of the grease crystallites on the stretched rubber is therefore likely to be such that one or other of



- (b) Orientation C.
 100 atom row in normal hydrocarbon coincides with 001 atom row in rubber.
 Compare Figs. 9b and 10b.



- (c) Orientations A and B.
 130 atom row in normal hydrocarbon coincides with 001 atom row in rubber.
 Compare Fig. 10c.



- (d) Orientations Y and Z.
 110 atom row in normal hydrocarbon coincides with 001 atom row in rubber.

Figure 11, (b - d). Anticipated patterns (diagrammatic) from various azimuthal orientations of normal hydrocarbons on stretched rubber.

the atom rows $[100]$, $[\frac{1}{2} \frac{\sqrt{3}}{2} 0]$ or $[110]$ coincides with the $[001]$ direction in the rubber, and analysis of the observed arc patterns has shown this to be the case.

The combined rubber and normal hydrocarbon patterns to be anticipated from the three types of orientation are shown in Figures 11 b, c, and d. The reciprocal lattice frameworks are also included to illustrate the geometric arrangement of the crystallites, but in order to avoid the confusion of too many lines, only even order lattice rows are shown.

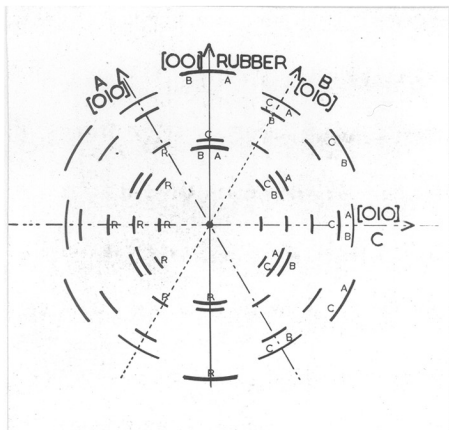
Figure 11b, in which the $[100]$ atom row coincides with the rubber $[001]$ direction gives the simplest pattern and is similar to the observed pattern of Figure 10b except that the latter also shows some random azimuthal orientation. It is also the case already discussed in relation to the low temperature work.

Figure 11c shows the pattern to be anticipated when the $[130]$ direction in the normal hydrocarbon coincides with the rubber $[001]$ axis, and it is seen to correspond to the observed pattern shown in Figure 10c. There are obviously two equally probable orientations according to whether the $[130]$ or the $[\bar{1}\bar{3}0]$ atom row takes the favoured direction, and in order to give the observed symmetry about the c axis of the rubber (Figure 10c) both must occur, as shown in Figure 11c.

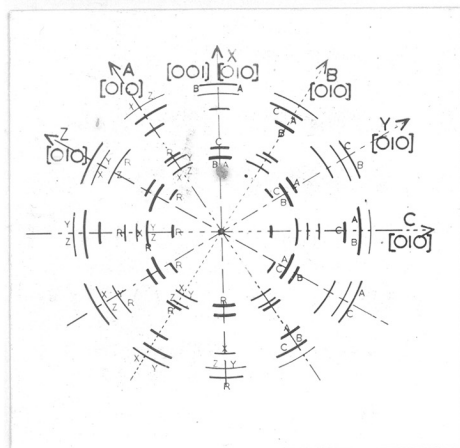
The pattern to be anticipated when the [110] direction in the grease crystallites coincides with the rubber [001] axis is shown in Figure 11d. As with Figure 11c, there are two equally probable orientations and both are shown. None of the observed patterns shows this arrangement alone, but it occurs as one component among the multiple orientations of Figure 10f.

The direction of the c axis of the rubber is subject to an angular spread of some $\pm 5^\circ$ about its mean position. There is consequently a similar tolerance in the mean direction of the hydrocarbon atom rows associated with it, and it appears from the experimental patterns that they do, in fact, take up positions slightly displaced from the mean axial direction of the rubber. Thus, although the inclination of the b axis of the normal hydrocarbon to its [130] direction is only 26° (Figure 11a) its inclination to the mean direction of the rubber c axis in Figure 10c is approximately 30° (see Figure 11c). That is to say, the mean [130] direction in the hydrocarbon is displaced by 4° from the mean c axial direction in the rubber. A similar displacement of the [110] direction is indicated in Figure 11d making the inclination of the b hydrocarbon axis to the mean c direction of the rubber 60° instead of 56° .

These slight displacements are probably related to the



(e) Orientations A,B,C.
Compare Fig. 10d.



(f) Orientations A,B,C,X,Y,Z.
Compare Fig.10e.

Figure 11,(e,f). Anticipated patterns (diagrammatic) from various combinations of azimuthal orientations of normal hydrocarbons on stretched rubber.

twinning properties of the normal hydrocarbons; for it has been observed (Brummage, 1947) that they are subject to a form of twinning in which the mean directions of corresponding axes are at 120° to one another. The angle between the $[110]$ and $[100]$ axes in a single crystal is only 56° (or 124°) and that between the $[110]$ and $[\bar{1}\bar{1}0]$ axes 64° (or 116°), but the angular spread indicated by the arcs in the grease pattern is of the same order, + 5° , as that observed for rubber and makes twinning of this type readily understandable.

It is obviously this twinning property of the hydrocarbons which gives rise to patterns of the type shown in Figures 10d and e. In the case of Figure 10d it would appear that the first layer of crystallites is associated with the rubber in one or other of the ways illustrated in Figures 11b and c and subsequent layers arrange themselves according to the twinning properties of the hydrocarbon. Since the three orientations of Figures 11b and c form a set in which the mean directions of corresponding axes are at 60° to one another, it is not possible to distinguish which type is directly associated with the rubber; the combined pattern, however, (Figure 11e) agrees well with that observed (Figure 10d).

The pattern illustrated in Figure 10e is rather more complicated. The azimuthal orientation is less complete

than in the foregoing cases, some degree of random orientation being indicated by the continuous (110) ring. There are, however, more intense regions on this ring which, when taken in conjunction with the rest of the arc pattern, indicate no less than six preferred orientations. The pattern appears to arise from a set of three groups of crystallites arranged as in Figure 11e, plus a second similar set of twinned crystallites displaced 30° from the first and giving rise to rather weaker diffractions. Of this second set, two of the patterns correspond to the arrangement shown in Figure 11d, suggesting a coincidence at the interface of atom rows of the $[110]$ or $[\bar{1}\bar{1}0]$ type with the rubber $[001]$ direction. The anticipated pattern, with the six orientations is shown in Figure 11f, and has similar characteristics to the observed pattern, Figure 10e.

Discussion.

The experiments described in this Section constitute a digression from the main theme of this work and have therefore not been carried further at the present time. It is hoped, however, to continue them later. All that can be said of these preliminary experiments is that they illustrate clearly that the rubber behaves as an active substrate strongly influencing the orientation of deposited layers of certain long chain hydrocarbons. In so far as they go, the results

confirm the structure of rubber as determined by direct diffraction methods.

A more extensive study of orientation effects in hydrocarbons and other materials deposited on rubber should be well worth while.

GUTTA PERCHA.

1. Introduction.

Gutta Percha and Balata are naturally occurring substances obtained like natural rubber from the latexes of certain trees indigenous to the African jungles. Although the botanical species from which the two are obtained are different both contain the same long-chain polymer of isoprene. This hydrocarbon is mixed with other materials classified as resins, dirt, and water; balata generally speaking, contains a much higher percentage of resins which makes it commercially inferior to gutta percha. Although it is a polymer of isoprene the purified hydrocarbon from gutta percha or balata has quite different mechanical properties from the natural rubber hydrocarbon, being tough and hornlike at room temperatures, exhibiting strongly thermoplastic properties and being quite devoid of rubber-like extensibility. Meyer and Mark (1930) have suggested that the gutta percha hydrocarbon is the trans -isomer of polyisoprene while natural rubber is the cis -isomer, and this is now generally accepted as the true explanation of the difference in their physical properties.

The chief properties of gutta percha which are of

practical importance are its thermoplasticity, chemical inertness, good insulating properties, and its extremely low water absorption. These combine to make it a valuable material for the insulation of submarine cables and its discovery contributed greatly to the rapid development of submarine telegraphy during the latter half of the last century. One disadvantage is its strong tendency to oxidise, though this can be largely counteracted by the use of antioxidants.

The first X-ray patterns of gutta percha and balata were obtained separately by Clark and Ott in 1926. Since then a number of workers have contributed to knowledge in this field. Owing to the ability of the material to crystallise in different forms, however, some aspects of the question of its structure still remain to be settled.

2. Literature.

The work of Clark and Ott referred to above established that balata and gutta percha, unlike natural rubber, showed crystalline interferences at room temperature even in the unstretched state, but the diffraction patterns of the two materials appeared to differ, which was surprising in view of the fact that their hydrocarbon constituent had been thought to be identical. In the following year Hauser (1927)

reported experiments in which gutta percha and balata were again found to give different patterns in the unstretched state, although the patterns from the stretched material were identical. A few years later, however, von Susich, working in collaboration with Hopff (1930) and Hauser (1931) clarified the situation considerably by demonstrating that gutta percha could be made to give either of the two patterns according to its previous heat treatment. These workers further showed that the hydrocarbon was the only crystalline constituent in the material so that for purposes of X-ray analysis it was immaterial whether one worked with purified or crude gutta percha. Shortly afterwards Dean (1932) also demonstrated a change in the plastic properties of the material which could be brought about by similar heat treatment. It thus appeared that this was a case of polymorphism. Stilwell and Clark (1931) observed similar effects to von Susich and his collaborators, but preferred to explain them on the basis of a second crystalline component which, they believed, became dispersed in the matrix at the transition temperature in so finely a divided state that it could not produce a diffraction pattern. The weight of evidence, however, appears to be strongly in favour of the theory of polymorphism.

The conclusions of these various workers may be summarised as follows: The gutta percha hydrocarbon as first extracted from the tree exists in a certain crystalline form

which has been termed the α -modification, and which gives a characteristic X-ray ring pattern showing three very strong rings at spacings of approximately 4.9A., 3.7A., and 3.3A. When the material is heated above a certain transition temperature it changes over to a second form termed the β -modification. The evidence as to the precise transition temperature and its dependence on the percentage of resins is somewhat conflicting, but the most probable value seems to be in the region of 65°C. The β -modification is amorphous at temperatures above the transition point but crystallises on cooling to give a material having a characteristic X-ray pattern with two strong rings at spacings of 4.7A. and 3.9A. Hauser and Susich (1931) found that both materials gave fibre diagrams in the stretched state, with identity periods of 8.8A. (α) and 4.9A. (β) along the fibre axis. Dean (1932) reports that the β -modification is transformed back to the α -form when maintained at a temperature a little below the transition point for a period of one to two hours; it thus appears that the α -form is the one which is genuinely stable at room temperature but the transformation velocity from the β to the α -form is so slow at this temperature as to be negligible so that the β -modification continues to exist in a meta-stable condition. Von Susich (1930), however, finds that the α -form can be recovered by dissolving the β material

in a suitable solvent and recrystallising, a point which is of some interest in connection with electron diffraction work where the material is usually deposited from solution prior to examination.

Since purification and manufacturing processes always involve the application of heat it is the β -modification which is more commonly met with in practice, and for this reason it has been much the more extensively studied. Thus Fuller (1936) in researches on the effect of vulcanisation on the X-ray pattern of gutta percha has proposed an orthorhombic unit cell for the β -form, with axial lengths of $a = 15.70$ or 7.85\AA ., $b = 11.9\text{\AA}$., c (chain axis) = 9.54\AA .. He finds this to be in agreement with a plane chain structure in which the isoprene units take the trans form in relation to the double bonds and the methyl groups are considerably displaced out of the main plane. He considers the two unit identity period of 9.45\AA . with the methyl groups lying on alternate sides of the chain more probable but his results do not rigidly exclude the one unit period of 4.77\AA . with methyl groups all on the same side of the chain. Storcks (1938), using electron diffraction, has obtained results which are in close agreement with Fuller's work, and has further demonstrated the interesting point that the crystalline regions show orientation with the c axis perpendicular to

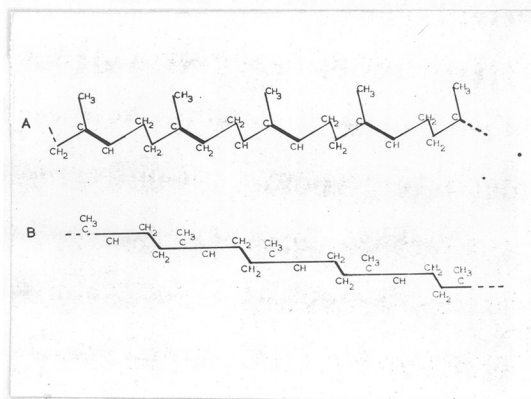


Figure 12.

β -Gutta Percha molecule - Diagrammatic.

- A. Projection in plane of double bonds.
- B. Projection perpendicular to double bonds.

the plane of the specimen although the film thickness (200A) was several times smaller than the generally accepted average length of the molecule (3,000A.).

The most complete analysis of β -gutta percha available so far is due to Bunn (1942) who has investigated the intensity distribution in his fibre diagrams and by applying the method of trial and error has been able to allocate positions to the carbon atoms in such a way as not to conflict with any observed facts. Bunn's unit cell is orthorhombic with $a = 7.85\text{A.}$, $b = 11.9\text{A.}$, $c = 4.72\text{A.}$, and space group $P2_12_12_1$; he finds that the isoprene units take the trans form in relation to the double bonds; the chain units of each isoprene unit are planar but successive units are displaced so as to form a series of steps (see Figure 12); thus they may be said to take the trans form in relation to the single bond $\text{CH}_2\text{-CH}_2$ connecting links between units. In order finally to satisfy his experimental intensities Bunn found it necessary to change certain bond lengths and angles from their previously generally accepted values. Jeffrey (1944) has, however, reexamined Bunn's results and considers that the intensities can be as well satisfied without this change.

Data regarding the α -modification is comparatively scarce and the only workers who appear to have attempted to

define all three axial lengths are Bruni and Natta (1934) who examined thin films by electron diffraction, and propose an orthorhombic cell for which $a = 6.53\text{\AA}$., $b = 7.68\text{\AA}$., $c = 9.60$ or 4.80\AA . The information on which they base this cell is somewhat limited, because they used the material solely in the unstretched condition and examined it in one orientation only. As Fuller pointed out, their value of the identity period is very different from the value of 8.8\AA . which Hauser and von Susich obtained from well oriented fibre diagrams. Nevertheless, Bruni and Natta's proposed constants are undoubtedly in close agreement with all the rings they observed.

In his work on vulcanisation referred to above, Fuller noticed that certain of his unvulcanised samples showed, in addition to the normal β -fibre-diagrams, a pattern similar to that ascribed by Hauser and von Susich to the extended α -form. He listed the spacings observed in this secondary pattern and found that there were discrepancies in the identity period as deduced from the different spots. This led him to suggest that there may be more than one crystalline form contributing to this so-called α -pattern, although he regarded his information as too limited to permit any attempt at defining the lattice constants. The suggestion is interesting, particularly when taken in

conjunction with the discrepancy in identity period between Bruni and Natta on the one hand and Hauser and von Susich on the other; it has been considered further in the present work.

It is also of interest to note that Bunn, in a general discussion on the forms which a trans polyisoprene chain might be expected to take up, predicted the existence of three forms of gutta percha. The first and simplest is the β -form described above in which the units are trans in relation to the single bonds and the methyl groups are all on the same side of the double bonds giving the identity period 4.72A.; the second is similar, except that alternate units are rotated through 180° about the fibre axis, so that methyl groups project alternately on either side of the chain thus requiring the double identity period of 9.4A., while the third possibility has its methyl groups all on the same side of the double bonds, but takes the cis form in relation to the single bond connecting links; this has a two unit identity period which Bunn computed as 8.9A. All other methods of combining the units are precluded, either because they form complex spiral molecules or on account of conditions of steric hindrance. The actual values of these identity periods are of course dependent on the angle which the connecting links make with the plane of the units, and Bunn

has selected this so as to give his observed value for the identity period of the β -molecule. The similarity of this predicted value of 9.4A. to the axial length of 9.5A. found by Bruni and Hatta would appear to be significant.

3. Present Work.

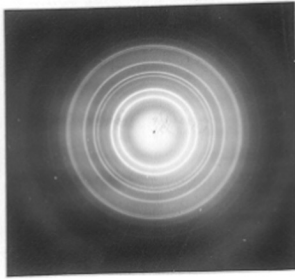
a) Experimental.

It was with this background in mind that the present examination of the arc pattern of gutta percha was undertaken.

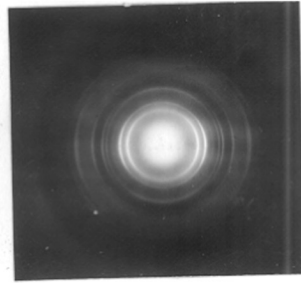
The material used was a commercial purified grade of gutta percha and, since the electron diffraction was in the first instance purely exploratory, no particular treatment was given to the material prior to examination.

The procedure for the preparation and examination of the specimens was similar to that described for natural rubber but the films were more brittle and inclined to tear than natural rubber films and the maximum extension which could be achieved was about 300%. Extension was helped by warming the substrate water to about 30°C. It was necessary to work with freshly made solutions and to examine the films immediately after deposition on account of their great tendency to oxidise. Films used for stretched specimens had a thickness of approximately 1,000A. prior to stretching, while the most suitable thickness for films examined in the

F3088

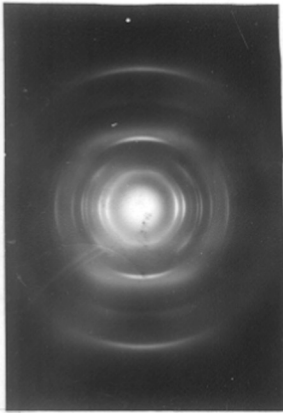


F3089



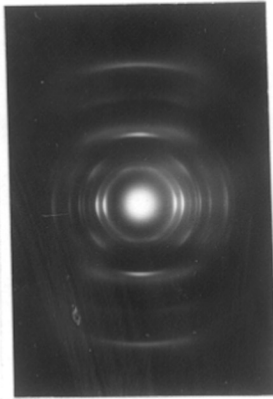
a) Unstretched. Film perpendicular to beam

b) Unstretched. Film inclined 45° to beam



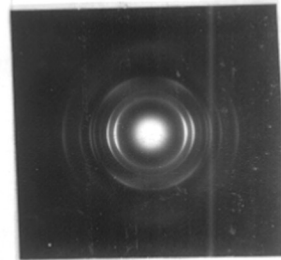
c) Stretched 300%
Film perpendicular
to the beam.

F3111



d) Stretched 300%
Film inclined
45° to beam

F3112



e) Stretched 300%
Orientation
axis inclined
45° to beam

F3113

Figure 13

Patterns obtained from β -gutta percha

unstretched condition was of the order of 200 - 300 Å. These thicknesses were estimated from the interference colours observed under oblique illumination.

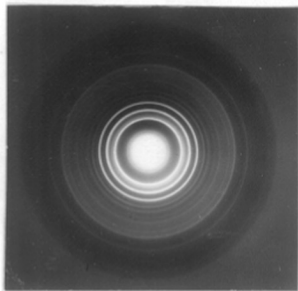
Absolute values of the spacings were obtained by direct comparison with graphite (Finch and Fordham, 1936).

4. Experimental Results.

The first point which emerged was that from a number of unstretched films examined at different times two quite separate and distinct types of pattern were obtained, although the materials were all from the same source and had, as far as was known, been treated in the same way. On the other hand no such distinction was observed between different stretched samples which all gave patterns of the same general type.

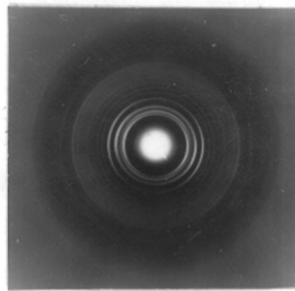
Two such series taken at different times are illustrated in Figures 13 and 14 of which Figures 13a and b and 14a and b refer to unstretched films and Figures 13 c-e and 14 c-d to stretched films. The experimental conditions were not adapted for the examination of the same films in the stretched and unstretched state but patterns of type 13 c-e were obtained from films taken from a solution which provided unstretched films giving patterns of type 13a both before and after the stretched film had been extracted, and

F3205

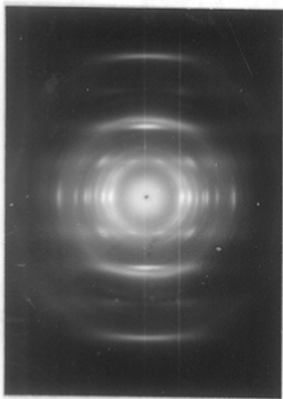


a) Unstretched. Film perpendicular to beam.

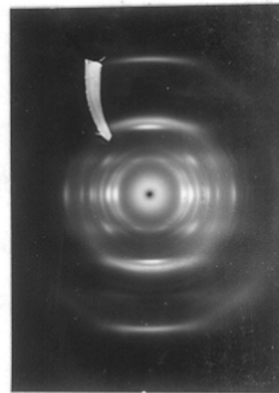
F3206.



b) Unstretched. Film inclined at 45 to beam.



c) Stretched 300%. Film perpendicular to beam. F3224



d) Stretched 300%. Film at 45 to beam. F3225.

Figure 14.

Patterns from Gutta Percha samples showing α -form when unstretched, and mixed β and γ forms when stretched.

patterns 14 c-d stood in the same relation to Figure 14a.

Inspection of these patterns, even before detailed measurement, reveals certain definite characteristics which are summarised below:-

1. Unstretched films give rise to one or other of two quite distinct crystalline diffraction patterns.

2. Both these crystalline arrangements show considerable orientation in the plane of the gutta percha film as is indicated by the arcing which occurs when the film is inclined to the electron beam.

3. Stretched films all give rise to one general type of pattern.

4. This pattern is composite. Its strongest arcs conform to the usual X-ray type of fibre or partial rotation pattern in which all the arcs lie on evenly spaced lines perpendicular to the direction of extension of the film. The equatorial arcs in this pattern appear to be very similarly spaced to the rings in pattern 13a. The subsidiary pattern shows arcs at intermediate spacings in the direction of extension. Its intensity in relation to that of the principal pattern varies somewhat from one specimen to another and, in one case, Figure 14c, it was found to show an angular displacement of about 2° from the principal pattern; thus it evidently arises from a different part of the specimen.

The subsidiary pattern must therefore be due to either a different crystal orientation or to a different crystalline form.

From these observations we may at once conclude that there are at least two crystalline forms and possibly three, since it is by no means established that the subsidiary pattern in the stretched samples corresponds to either of the two patterns occurring for the unstretched material and, secondly, that the treatment involved in producing the stretched test pieces precludes the formation of a material which has wholly or largely the crystalline form of Figure 14a but is favourable to the formation of material of type 13a.

It may be mentioned that although the experiments so far have not shown what conditions favour the formation in the unstretched films of one crystalline form or the other, it was found that the second form could be largely inhibited by treating the solid material in air at about 90°C. for half an hour immediately prior to making the solution. The specimens which yielded the patterns of Figure 13 were in fact prepared in this way, although there were several others which gave similar patterns without this treatment.

At this stage it is necessary to examine the patterns in more detail. The spacings for the two ring patterns (Figures 13a and 14a) are therefore set out in Table 6. The

results shown are the means from four or five different patterns; the absolute values were obtained for the sharpest rings by comparison with the graphite 1.228 kx spacing (Finch and Fordham, 1936; Trzebiatowski, 1937; Nelson and Riley, 1945).

Various published figures are also quoted in Table 6, and it will be seen at once that the pattern of Figure 13a corresponds to the normal β -modification while Figure 14a with its three characteristic strong rings corresponds to what has been termed the α -modification.

The various patterns will therefore be considered individually in what follows in an attempt to gather all the possible information on the crystal forms. The equatorial spacings of the principal pattern in the stretched material were found to correspond very closely with the ring spacings of the β -pattern and consequently the two patterns are considered jointly in relation to the structure of the β -modification. No such correspondence was observed between the subsidiary pattern in the stretched materials and the ring pattern of Figure 14a, and the two are therefore considered separately. When dealing with a case of polymorphism it is of course highly probable that the material is always to some extent a mixture with one or other form predominating. This is fairly obviously the

Table 6.

Ring Pattern of Figure 13a.

Observed spacing kx. (Relative to graphite(110) =1.228 kx)	Published Results for β -modification.			
	Hopff and Susich (1930) A.	Hauser and Susich (1931) A.	Fuller (1936) (equatorial arcs of fibre diagram) A.	Storks(1938) (electron diffraction) A.
w 1.58				1.18
w 1.77				1.76
m 1.92				1.91
mw 1.97			m 1.95 vw 2.02	1.97 2.04
m 2.38			vw 2.12 s 2.37	2.17 2.38
m 2.78	w 2.77		s 2.78	2.75
mw 2.97	m 2.95		m 2.98	2.96
vw 3.35	vw 3.29		vw 3.15	3.32
vs 3.91	s 3.89 m 3.90	3.9	vs 3.91	3.87
vs 4.72	m 4.75 vs 4.73	4.8	vvs 4.73	4.71
			+ longer spacings	

w = weak; m = medium; s = strong; v = very.

Table 6.

Ring Pattern of Figure 14a.

Observed spacing kx. (Relative to graphite(110) =1.228 kx)		Published Results for α -modification.			
		Hopff and Susich (1930) A.	Hauser and Susich (1931) A.	Fuller (1936) (equatorial arcs of fibre diagram) A.	Bruni and Natta (1934) (electron diffraction) A.
m	1.65				mw 1.24 w 1.64
ms	1.89				mw 1.90
vw	2.03				vw 2.04
w	2.29				vw 2.22
vw	2.47				vw 2.42 vw 2.48
mw	2.72	w 2.74			w 2.69
mw	2.94	w 2.98	(approx.)		mw 2.95
vs	3.35	s 3.32	3.3	3.33	s 3.28
vs	3.94	s 3.94	3.9	3.91	vs 3.86
vs	4.94	s 4.56 vs 4.96 m 4.97		4.95	vs 4.82
m	7.89		7.7	7.91	
		vw 12.2			

case in the stretched material; it is less obvious in the unstretched patterns but occurs to some extent; thus, for instance, the faint ring of spacing 3.35 kx. in Figure 13a most probably arises from a trace of the α modification in which this spacing comes up very strongly; other such cases will probably be observed.

5. Lattice Constants of the β -modification (Figures 13a-e and 14a-d).

The structure of β -gutta percha has already been extensively studied and the present work can only be regarded as a check on agreement with previous work.

The lattice constants proposed by Bunn (1942) and Fuller (1936) were used as a guide in indexing the observed arcs and the axial lengths were then calculated from the measured radii. The unit cell thus determined was orthorhombic and had axial lengths $a = 7.82$ kx., $b = 11.85$ kx., $c = 4.74$ kx., or, multiplying these values by 1.002 to give Angstrom units, $a = 7.84\text{\AA}$., $b = 11.87\text{\AA}$., $c = 4.75\text{\AA}$.. Full details of the results are given in Table 7, and it will be seen that the agreement is in general very good.

The indices of the non-axial arcs from the inclined films were in the first instance assessed purely by finding computed spacings of similar magnitude, but later some further check was applied by relating their angular separation to the angle of inclination of the film.

Table 7.

a). Unstretched material. Figures 13a, b.

	Observed spacing kx. (Relative to graphite(110) =1.228 kx.	Indices suggested (hkl)	Spacing computed for a = 7.82 kx. b = 11.85 kx. c = 4.74 kx.
Specimen perpendicular to beam.	4.72	120	4.72
	3.91	200	3.91
	2.97	040	2.96
	2.78	{230	{2.78
		{140	
	2.38	320	2.39
	1.97	400	1.96
		340	1.96
1.92	410	1.93	
1.77	430	1.75	

Specimen
inclined 45°
to beam.Spacings along diameter parallel to axis
of inclination were as above.

Other arcs:

2.95	201	3.03
	211	2.92
2.26	301	2.28
1.79	401	1.81
	341	1.81

For further details regarding these arcs see
Table 8.

Table 7. (continued)

b) Stretched material. Figures 13c,d and 14 c,d.

(only those arcs referring to the β -modification are included here. For full consideration of the composite pattern, see Figure 16c).

	Observed spacing kx. (Relative to graphite (110) = 1.228 kx.)	Indices suggested (hkl)	Spacing computed for a = 7.82 kx. b = 11.85 kx. c = 4.74 kx.
Equatorial arcs	1.93	410	1.93
	2.38	320	2.39
	2.77	{230 140}	{2.78 2.77}
	2.97	040	2.96
	3.91	200	3.91
	4.72	120	4.72
First layer line.	1.80	{411 401 341}	{1.79 1.81 1.81}
	2.26	{311 301}	{2.24 2.28}
	2.97	211	2.92
	4.43	011	4.40
	Second layer line.	2.37	002
Third layer line.	1.57	003	1.58
	1.52	113	1.54
Fourth layer line.	1.19	004	1.18

The pattern for the fibre axis inclined to the beam has the same equatorial arcs as above (Figure 13e).

All the rings which appear in the pattern from an unstretched film of material with the beam at normal incidence (Figure 13a) can be indexed as $hk0$ rings thus indicating that the crystals are oriented with their c axes perpendicular to the film plane. This is in accord with the observations of Storks (1938) and is, as he pointed out, somewhat surprising since the thickness of the film (~ 200 A.) is many times less than the generally postulated length of a single molecular chain (3,000 A. approx.). A similar phenomenon was observed by Charlesby (1945) in work on thin films of polythene. Storks therefore suggests that the long chains take up a zig-zag concertina-like formation such that chain segments between the folds are nearly perpendicular to the film; this is not an unreasonable assumption since the deviation from the truly perpendicular arrangement of the chain segments in relation to the film surface need only be small and well within the limits permitted by the angular spread of the arcs of the inclined film (Figure 13b). On this assumption, stretching the specimen would involve a drawing out of the concertina into its fully extended form, possibly combined with a sliding of adjacent chains or crystalline regions relative to one another. The suggestion is of particular interest in connection with a claim made by G.Pankow (1936) to have observed a long spacing of 115A. in the direction of the orientation axis in stretched specimens

examined by X-rays. For, if the folded configuration is supposed to be quite general and not dependent on the use of thin films, then it could be readily understood that even the fully extended chain might show discontinuities at what might be termed the "fold-points" thus introducing a periodicity of the order observed by Pankow. In fact the most probable situation would be that the chains in the stretched material were in a very flat zig-zag configuration giving the effect of a slight spread in the orientation about the extension axis as indeed is in accord with the fact that the pattern consists not of spots but of arcs. This view, however, gives no indication as to why the length 115A. should be favoured for these chain segments.

From the foregoing observations it is apparent that β -gutta percha, unlike natural rubber does not require the application of a stretching force to bring about its crystallisation. The crystallites exist at random in the block of unstretched material and the effects of forming into thin films and stretching are merely to direct and control their orientation. The mechanism of the transformation from the unstretched to the stretched type

of orientation in thin films is open to discussion as indicated above, but from the point of view purely of the crystalline diffractions we have in the one case a group of crystallites randomly oriented about a common zone axis perpendicular to the film plane, and in the second a group of crystallites oriented about the same zone axis which, however, now lies in the plane of the film. Again the orientation about this axis (direction of stretch) is largely random since very little, if any, difference can be detected in the patterns when the films are inclined about this orientation axis (Figures 13c and d, and 14c and d). Consequently it would be anticipated that by suitable adjustment of the inclination of the films the two types of specimen could be made to give identical patterns, and comparison of Figures 13b and 13e show this to be the case. Figure 13b is from an unstretched film examined with the film plane (and therefore the zone axis perpendicular to it) inclined at 45° to the beam, and Figure 13e is from a stretched film examined with the axis of extension inclined at 45° to the beam. It will be seen that the two patterns show a marked similarity, such differences as do exist being readily understood since the inclination of the particular crystallites on which the beam impinges cannot be precisely determined on a wire gauze where portions of the film may

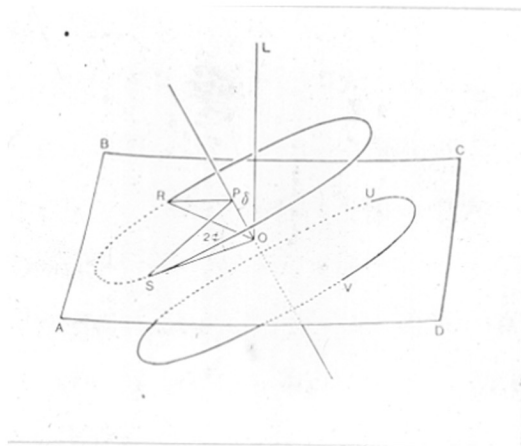


Figure 15.

always tend to sag between the meshes of the gauze.

The inclination of the beam to the specimen in these two cases can be estimated by the following method, which also affords a check on the indexing of the various arcs which occur only in the case of the inclined film. Thus, with orientation about a zone axis perpendicular to the plane of a transmission film, the angular separation of a pair of arcs appearing when the film is inclined to the beam is related to the angular inclination of the zone axis to the beam in a manner which can be deduced as follows.

Each of the rings occurring when the film is perpendicular to the beam (i.e. when the zone axis is in the reversed direction of the electron beam) will in general reduce to four arcs when this axis is inclined.

For, suppose ABCD (Figure 15) is an approximately plane portion of the Ewald sphere; LO, the direction of the incident beam; O, the point in which the undeflected beam strikes the sphere; OP the direction of the inclined zone axis [001], and P the point (001) of the reciprocal lattice for all the contributing crystals.

Then the other points (hkl) giving rise to the deflections considered lie on circles with their centres on OP and in planes normal to it.

But any such circle will cut the portion of the Ewald

sphere in two points R, S and since the reciprocal lattice has a point of symmetry at O, there will be two similar points U, V diametrically opposed to S and R respectively.

Now if 2ϕ is the angular separation of R, S and δ is the inclination of OP to OL,

$$\cos \widehat{SOP} = \sin \delta \cos \phi$$

But \widehat{SOP} is, by definition, the angle between the zone axis [001] and the normal to the hkl plane giving rise to the reflections considered; hence

$$\begin{aligned} \cos \widehat{SOP} &= (h/a + k/b + l/c) \wedge (0/a + 0/b + 1/c) / (OP \cdot OS) \\ &= \left[(h \times 0/a)^2 + (k \times 0/b)^2 + (1 \times 1/c^2) \right] / (OP \cdot OS) \end{aligned}$$

But OP and OS are respectively the reciprocal spacings of the (001) and (hkl) planes

$$\begin{aligned} \cos \widehat{SOP} &= (1/c^2) \cdot d_{(hkl)} \cdot d_{(001)} \\ &= (1/c^2) \cdot d_{(hkl)} \cdot c \end{aligned}$$

$$\cos \phi \sin \delta = d_{hkl}/c$$

Applying this relationship to the observed data for Figures 13b and 13a we have the results set out in Table 8 from which it is seen that the angular inclination of the orientation axis to the beam is approximately 39° for the unstretched specimen (Figure 13b) and 50° for the stretched

specimen, both of which are quite reasonable figures since the inclination of the film as a whole was approximately 45° in both cases. It can also be readily shown that any value of the l index other than unity would lead to impossible results requiring $\sin \delta > 1$. The method does not, however, afford any check on the other indices since the zone axis was one of the principal crystal axes.

Table 8.

	Observed spacing kx^*	Semi-angular separation ϕ	$\cos \phi$	Proposed hkl	$\sin \delta = \frac{1d}{4.72} = \frac{1}{\cos \phi}$	
Fig.13b	2.94	10°	0.98	201or211	0.63	39°
	2.26	40°	0.77	301	0.62	38°
	1.79	54°	0.59	401or341	0.64	40°
Fig.13e	2.94	34°	0.83	201or211	0.75	49°
	2.26	53°	0.60	301	0.79	52°
	1.80	62°	0.48	401or341	0.79	52°

* Relative to graphite (110) = 1.228 kx .

All the observed data are thus seen to be in accord with the lattice constants and type of orientation postulated in the foregoing discussion.

6. Patterns of Figures 14a and 14b - α -Gutta Percha.

The spacings of the rings in Figure 14a correspond closely to those observed by Bruni and Natta (1934) in their electron-diffraction study of gutta percha (see Table 6), and

consequently some consideration of the unit cell which they proposed seemed expedient. The essential characteristic of their indexing was that they supposed the three strong rings to be the first and second orders of the principal axial spacings and the cell to be orthorhombic; this scheme was therefore examined in relation to the present patterns. The result is indicated in Table 9 and it will be seen that it does in fact afford a very neat interpretation of all the observed spacings. The axial lengths of the cell thus arrived at are $\underline{a} = 6.70 \text{ kx.}$, $\underline{b} = 7.89 \text{ kx.}$, $\underline{c} = 9.89 \text{ kx.}$ Bruni and Natta's results did not enable them to distinguish between a cell of approximately this size ($\underline{a} = 6.53\text{A.}$, $\underline{b} = 7.68\text{A.}$, $\underline{c} = 9.60\text{A.}$) and one in which the \underline{c} axis takes the half value corresponding to a single isoprene unit, but in the present work the extra arc (111) which appears when the film is inclined to the beam definitely requires the double isoprene unit value.

The indices quoted first in the Table are those for which the computed and observed results show the best agreement. It is somewhat surprising, however, that the spacings (410) and (140) should appear rather than the higher orders (400) and (040) of the two very strong rings (200) and (020); it is possible that the latter indices may be the true ones, or that the rings are doublets; the

Table 9.

α -modification Unstretched material. Figures 14a, b.

	Observed spacing kx. (Relative to graphite (110) =1.228 kx.)	Indices suggested (hkl)	Spacing computed for a = 6.70 kx b = 7.89 kx c = 9.89 kx.
Specimen perpendicular to beam (Ring pattern of Fig.14a)	7.89	010	7.89
	4.94	002	4.94
	3.94	020	3.94
	3.35	200	3.35
	2.94	β , 040 (Table7) γ , 420 (Table11) γ , 040	
	2.72	202	2.77
	2.47	004, 130	2.47, 2.45
	2.29	222	2.27
	2.03	302	2.03
	1.89	140, 040	1.89, 1.97
1.65	410, 400	1.64, 1.67	
Specimen inclined 45° to beam. (Fig.14b)	Spacings along diameter parallel to the axis of inclination were as above.		
	The only extra arcs which appeared were two on the perpendicular diameter.		
	4.55	111	4.54
4.07	γ , 012 (Table11)	-	

great difference in intensity of the two orders might well explain the discrepancy in measurement.

The patterns taken with the specimen inclined to the beam showed pronounced arcing. All the spacings of the ring pattern obtained with the beam perpendicular to the specimen appear in Figure 14b as arcs on the diameter parallel to the axis of inclination, while two new spacings are indicated by arcs on the diameter perpendicular to this. There must therefore be some kind of orientation of the gutta percha crystallites perpendicular to the film plane. This orientation cannot, however, be of the same type as that occurring in the β -modification because none of the indices are consistently zero for all the spacings of the ring pattern (Table 9). On the other hand, with each diffraction one or other of these indices is always zero, and it would appear that we have here a mixture of three orientations, the crystals all having one or other of the three principal crystal axes oriented perpendicular to the film plane. This state of affairs is probably related to the fact that the three axial lengths do not differ greatly, so that a mixed type of packing would be fairly easily attained. It is, however, most unusual to find such a mixed orientation for a long-chain polymer, as the chain axis usually governs the orientation in such cases; it would appear that the chain axis plays a less

dominant role in this α form of gutta percha than in most rubber-like plastics. These observations may well have some bearing on the fact that α -gutta percha does not appear to give fibre diagrams on stretching.

Summarising the present observations from this pattern it may be said that they can be completely interpreted on the basis of an orthorhombic unit cell with axial lengths $a = 6.70$ kx., $b = 7.89$ kx., $c = 9.89$ kx., and that the crystallites are arranged in the film so that one or other of the orthogonal axes is perpendicular to the film surfaces. The results are in general agreement with those of Bruni and Natta, though the axial lengths are slightly greater. The appearance of one extra arc in Figure 14b makes it possible to state definitely that the cell must have the two-unit identity period of 9.89 kx rather than the half value.

7. The Subsidiary Pattern in Stretched Specimens.
Figures 13c,d and 14c,d. γ -Gutta Percha.

As stated in an earlier section, all the patterns from stretched specimens appeared to be composite representing two different crystalline arrangements. The difference in relative intensity of the two patterns from different photographs and the slight angular separation which appeared in one of these photographs (Figure 14d) permitted the selection of ten arcs in each quadrant as belonging to the

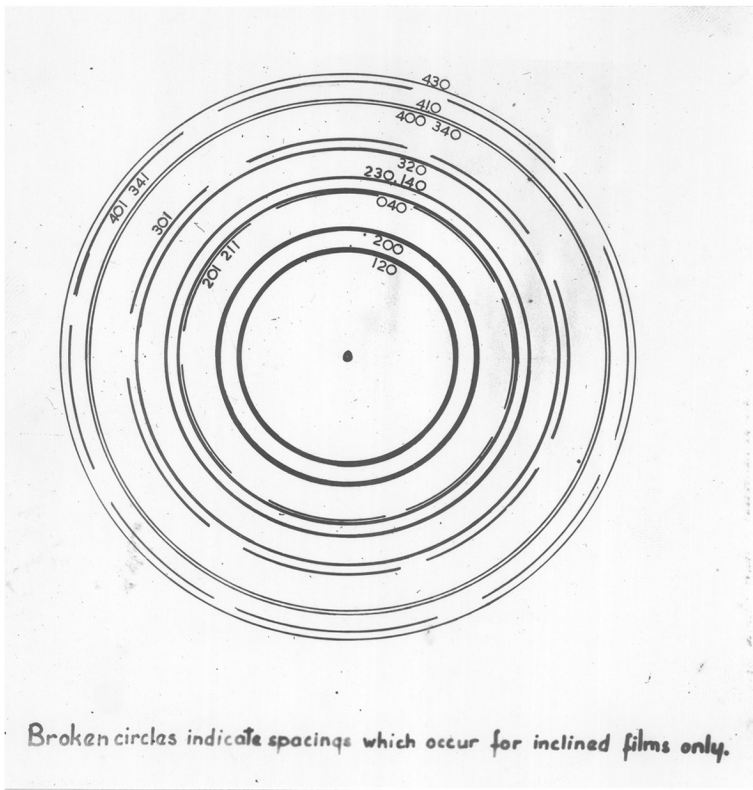


Figure 16a.

Ring pattern from unstretched β -gutta percha (diagrammatic).

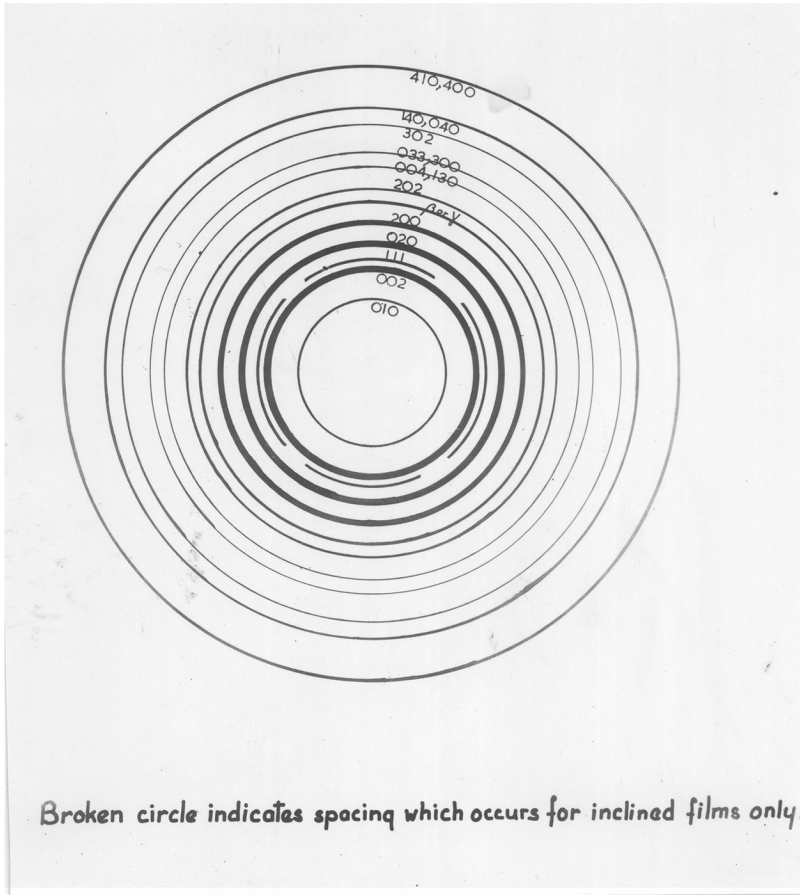


Figure 16b.

Ring pattern from unstretched α -gutta percha (diagrammatic).

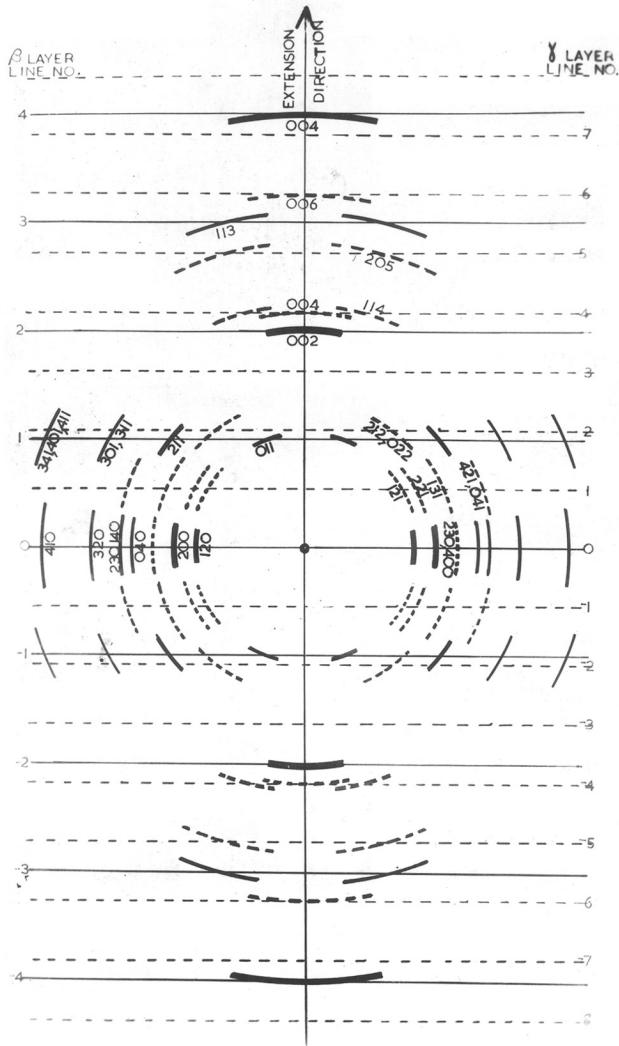


Figure 16c. Combined β and γ pattern from stretched gutta percha (diagrammatic).

γ arcs are shown dotted.

subsidiary pattern, and these are set out in Table 10.

Table 10.

γ -modification. Stretched material. Figures 13c,d, and
Figures 14c,d.

(Only those arcs belonging to the γ pattern are included here.

For full consideration of the composite pattern see Fig.16c.).

Specimen perpendicular to beam or inclined about fibre axis.	Observed spacing kx. (Relative to graphite(110) = 1.228 kx.	Indices suggested (hkl)	Spacing computed for a = 14.4 kx b = 11.55kx c = 8.74kx.	
Equatorial arcs.	3.35	400	3.35	
		230		
First layer line	4.54	121	4.53	
		221	3.91	
		301	3.98	
		3.35	131	3.41
		2.72	421 041	2.75 2.74
Second layer line.	3.48	212 022	3.49 3.48	
Fourth layer line	2.18	004	2.18	
		114	2.12	
Fifth layer line	1.67	205	1.69	
Sixth layer line	1.46	006	1.46	

Although the number of arcs is small, the high degree of orientation adds considerably to the information which is available from them, and it was found possible to derive a

probable unit cell by graphical methods.

The pattern is effectively a partial rotation diagram with the rotation axis in the direction of extension, and its form indicates that the other crystallographic axes are perpendicular to this direction at least to within the limits of about 2° set by the angular spread of the arcs. The identity period in the direction of extension is 8.74 kx which corresponds fairly well to the value of 8.8A. quoted by Hauser and von Susich (1931) and several of the spacings are similar to those quoted by Fuller (1936) for the subsidiary pattern which occurred in some of his fibre diagrams. It therefore seems evident that this is the crystalline form to which these workers have referred as the α -modification in their work on stretched material. Since only two types of gutta percha have been reported previously it was at first anticipated that this pattern and the ring pattern of Figure 14a would be found to arise from the same crystalline form, and attempts were made to fit both the patterns to the same axial framework. These, however, did not meet with success; on the other hand arcs appearing in the fibre diagram were found to fit very well with an orthorhombic unit cell having axial lengths $a = 13.40$ kx., $b = 11.55$ kx., $c = 8.74$ kx. It therefore appears to be highly probable that the patterns refer to two quite separate crystalline forms one of which occurs only in unstretched films and the other

principally in stretched films. If this is the case it would appear to bring into line much of the apparently contradictory evidence of previous workers. In the present work, therefore, the patterns of Figures 14a and b (unstretched material) which correspond to those which the earliest workers assigned to the α -modification and which do appear to arise from the entirely untreated material, have been termed the α patterns while those referring to the stretched material as described in the present section are termed the γ patterns. While it is easy to recognise by inspection, from which crystalline form some of the arcs in the composite β and γ patterns (Figures 13c,d and 14c, d) arise, this is not so with all the arcs, and a diagrammatic representation of the composite pattern is therefore appended (Figure 16c). This diagram shows how the arcs have been distributed between the two patterns and indicates the indices assigned to each. For the sake of completeness, diagrams of the two ring patterns are also included (Figures 16a and b).

One other point that should be noted is that although the whole pattern of Figures 14a and b could not be fitted into the proposed γ -lattice certain of the spacings could be so indexed. The alternative forms of indexing for these rings are set out in Table 11 and it will be noted that, in particular, the spacing 2.94 kx which gave poor agreement

with any calculated values for the α -pattern is within the experimental limits of accuracy for either the (420) or (040) spacing of the γ arrangement; on the other hand it could be indexed as (040) of the β -pattern. Thus it is possible that the γ arrangement may be present in some of the unstretched material but remain undetected on account of the similarity of its principal spacings to those of the other two modifications.

Table 11.

Alternative forms of indexing for certain rings
of Patterns 14a and b.

Observed spacing. kx. (Relative to graphite (110) =1.228 kx.)	α cell a = 6.70, b = 7.89 c = 9.89 kx.	Indices (hkl)	computed spacing	γ cell a = 14.40, b = 11.55, c = 8.74 kx.	indices (hkl)	computed spacing
3.94		020	3.94		{030	3.85
3.35		200	3.35		{221	3.91
2.94					400	3.35
2.47		{004	{2.47		{420	2.90
2.29		{130	{2.45		{040	2.89
4.06		222	2.27		340	2.42
4.55	Fig. 14b only	111	4.54		502	2.28
					012	4.09
					121	4.53

8. Discussion.

The examination of β -gutta percha has, as was anticipated, given results in general accord with those of previous workers. Consequently there is little that requires comment, except to emphasise the point originally made by Storks (1938) that the orientation of the crystallites perpendicular to the film surface in films whose mean thickness is less than the accepted length of the chain may denote discontinuities within the single molecular chain; this is especially interesting when considered in conjunction with Pankow's claim (1936) to have observed a long spacing of 115A. in the stretched material.

In relation to the other modifications of gutta percha these results are more illuminating leading as they do to the identification of two possible forms besides the β -form. The existence of two such forms was suspected by Fuller as a result of his work on stretched gutta percha at various stages of vulcanisation and was predicted by Bunn as a result of his theoretical consideration of the possible configuration of a trans polyisoprene chain. Furthermore the two identity periods observed (9.9 kx. and 8.7 kx.) are in good qualitative agreement with those predicted by Bunn (9.4A. and 8.8A.). Thus it would appear that although the experimental data obtained in the present work is admittedly limited it does,

when taken in conjunction with the information already available, constitute strong evidence in favour of the existence of these two forms.

If the existence of these two forms is accepted, it is of interest to consider why the unstretched condition should favour one and the stretched condition the other. According to Bunn's hypothesis both the β and γ forms* have molecular arrangements in which all methyl groups lie on the same side of the main chain while the α form has them disposed on alternate sides of the chain. This provides one fundamental difference between the α form and the two others, and it appears feasible that the more highly ordered stretched condition would favour the former type of configuration. Moreover, the mixed type of orientation occurring in thin films of the α material again differentiates it from other long chain polymers and its inability to give a normal fibre diagram may well be associated with this.

It is obvious that some way must be found of obtaining patterns showing much fuller detail before these points can be finally settled. The present work at least appears to have opened up new possibilities and indicated lines along which further research may be prosecuted.

* The nomenclature here differs from that used by Bunn who has termed the material giving rise to the identity period of 8.8A. the α form and that with the anticipated period of 9.4A. the γ form.

POLYCHLOROPRENE.

1. Introduction.

The polychloroprene material used in these experiments was one of a series of synthetic products developed by the du Pont de Nemours Corp. of U.S.A., and known under the generic name of Neoprene. Chemically, the pure polymer is believed to be a long-chain compound similar to polyisoprene, except for the replacement of the methyl groups by chlorine atoms. It can be compounded and vulcanised although sulphur is not in this case a suitable vulcanising agent. The halogen substitution confers on the finished product a greatly improved resistance to oils and solvents which makes it superior to rubber for many purposes where contact with these is involved, although the products generally are not so resilient as those of natural rubber.

The material is not supplied in the form of the pure polymer but is available in a number of grades containing different combinations of many other ingredients including stabilisers, antioxidants, accelerators of vulcanisation, plasticisers, etc., intended to make the products specially suitable for a variety of different purposes. The material used in the present experiments was the general purpose grade known as Neoprene GN. It was not preplasticised and is

available in the form of rods which can be cut with a knife. It is very slowly soluble in benzene and more readily soluble in trichlorethylene.

The structure of Neoprene has been studied by means of X-rays by Clews (1942) and Bunn (1942) in this country, while Kruirow (1935) in Leningrad has examined Neoprene and a similar Russian product by electron diffraction. Both Clews and Bunn found that the material was amorphous in the unstretched state but gave rise to crystalline interferences on stretching. The crystallisation produced on stretching was, however, far less well developed than was the case with natural rubber, and the background intensity was relatively high. Kruirow, on the other hand, found crystalline interferences even in the unstretched state.

All three workers suggest orthorhombic unit cells for the polymer but the axial lengths suggested differ appreciably. Thus Bunn gives $a = 8.84\text{\AA}$., $b = 10.24\text{\AA}$., $c = 4.79\text{\AA}$., while Clews prefers $a = 8.90\text{\AA}$., $b = 12.21\text{\AA}$., $c = 4.70\text{\AA}$., and Kruirow gives the values of $a = 8.23\text{\AA}$., $b = 10.93\text{\AA}$., $c = 4.79\text{\AA}$.. Discrepancies are not surprising, for the crystalline diffractions are weak, diffuse, and few in number, and these are circumstances which lead at once to inaccuracies in measurement and ambiguities in the indexing of the diffractions. A further possibility which must not be overlooked is that

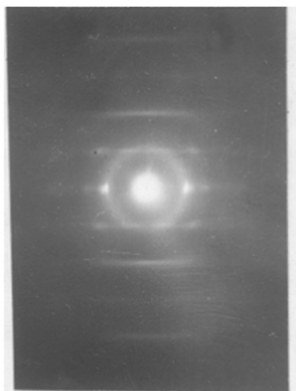
of polymorphism in the material. On the whole, however, density considerations make Clews' cell somewhat improbable, for although Clews himself considers this point, the figure of 1.086 which he quotes for the measured density is very different from that of 1.25 which is generally accepted. As with gutta percha and natural rubber, Bunn has carried the investigation a stage further than other workers and has deduced a possible atomic arrangement. He postulates a structure which is closely analogous to that found for gutta percha and is thus inherently possible.

The present work contributes little fresh data regarding the lattice constants but indicates an interesting difference between the molecular ordering which occurs when Neoprene is stretched and that observed for natural rubber.

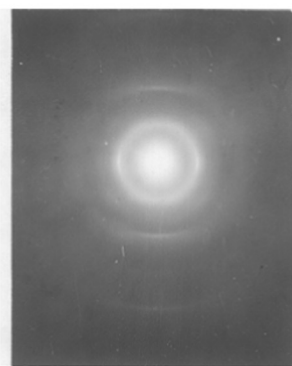
2. Experimental.

The specimens were prepared in the same way as those of natural rubber and gutta percha. Since the material was only slowly soluble in benzene an attempt was made to use films deposited from trichlorethylene solution but this proved unsuccessful on account of the high density of this solvent, and best results were obtained with benzene or benzene to which a few drops of trichlorethylene had been added.

The films did not spread so evenly as those of natural



(a) F2242



(b) F2289.

Figure 17.

Patterns from stretched polychloroprene.
Plane of film perpendicular to beam in both cases.

rubber or gutta percha and were less easy to manipulate. Furthermore, the material did not take up the ordered configuration ~~and~~ so readily and appeared to be more prone to exhibit relaxation when maintained in the extended condition, so that frequently, when the film was examined in the camera, no trace of crystallisation was observed, the resulting pattern exhibiting the haloes characteristic of the amorphous or disordered state. However, some patterns were obtained which did indicate molecular orientation. Experiments were made both with the material as received and with samples which had been extracted with hot acetone and softened by masticating on a rubber mill, but the best results were obtained with the untreated material.

3. Experimental Results.

Two of the clearer patterns exhibiting a considerable degree of crystallisation are illustrated in Figures 17a and 17b. While these are not comparable with the natural rubber patterns for clarity and profuseness of detail, they do illustrate in a somewhat striking manner certain differences between the type of orientation occurring in the two materials

This is particularly well brought out in Figure 17a; for the most obvious feature of this pattern is the series of straight lines running perpendicular to the direction of

extension. The pattern is thus reminiscent of the reflections obtained from the long chain hydrocarbons and is characteristic of a largely uni-dimensional ordering. In the case of Neoprene GN "crystallisation" in fact seems to consist mainly of an orientation of the long chains of the polymer in a common direction rather than of a grouping into like-oriented crystals or micelles.

A brief indication of the way in which these observed patterns could arise is given below. The argument follows generally similar lines to that given in relation to the diffuse zone pattern from natural rubber.

It is supposed that the molecules are all oriented with their chain axes in the direction of extension but are not otherwise related to one another. Each molecule consists of a series of identical chloroprene units repeated indefinitely along the chain and therefore has an identity period in this direction. Any diffraction maxima which occur must therefore lie on equally spaced "layer lines" perpendicular to this chain direction of the molecules. Since the molecules are not supposed to be crystallographically related to one another, interferences between diffractions from neighbouring molecules will not occur, but there will be variations in intensity along the layer lines, arising from the arrangement of the scattering centres within each

chloroprene unit.

The precise form of these intensity variations depends both on the atomic configuration of the chloroprene unit and its orientation about its own axis in relation to the electron beam. In Section II, on the similar case for natural rubber, calculations of these variations were made for two proposed configurations in one selected orientation, but the Neoprene patterns do not show any indication of a preferred orientation, and any such calculations would be correspondingly more complex. A similar problem has been investigated thoroughly for the case of certain of the normal hydrocarbons which have only two rows of atoms and whose structure is well understood, by Karle (1946) and Karle and Brockway (1947) who postulated various types of randomness in the arrangement of the long chains and examined the patterns to be expected. For our present purpose, however, it is sufficient to note that the pattern to be anticipated would comprise equally spaced lines with some variations in intensity along them, and that these are, in fact, the principal characteristics of the observed patterns.

This straight line pattern is, however, not the complete representation of the pattern from stretched polychloroprene for it is always associated with certain arcs which indicate a small degree of crystalline ordering.

Of these the strongest, and usually the first signs of ordering to appear, are the two equatorial arcs; there is also one set of arcs on the first 'layer line'; and in certain cases, two arcs further out on the equator can be detected.

A further point worthy of note in connection with the general characteristics of the patterns is that Figures 17a and b are seen to differ slightly although the experimental conditions were reproduced as closely as possible. Thus the straight lines of Figure 17a are curved in Figure 17b. In fact the unidirectional ordering is less perfect than in the previous case, and it would appear that there is an appreciable spread in the direction of the principal axis of the molecular chains. This variability was itself one of the characteristics of the polychloroprene material, the patterns being far less readily reproducible than was the case with natural rubber or gutta percha, and it may well be associated with its synthetic origin; for instance none of the samples examined in this work showed any signs of the crystalline form in the unstretched state as was observed by Krullow (1935) for both Russian and American manufactured polychloroprenes.

It is obviously impossible to derive the lattice constants of the crystalline arrangement from such scant

data, but such spacings as were observed did not show any wide divergences from those found by the X-ray workers. The identity period along the chain, as measured in terms of the applied accelerating voltage of the electron beam and the camera length, and one comparison pattern with palladium foil, is 4.70A.; the equatorial spacing is 4.4A., and the spacing of the arcs on the first layer line is 3.0A. On the basis of Bunn's cell with $a = 8.84A.$, $b = 10.24A.$, $c = 4.79A.$, the 4.4A. spacing could be indexed as the (200) and (120) arcs combined (4.43A. and 4.44A. respectively), and the 3.0A. spacing as (211) (3.10A.). While the degree of agreement is not high it is probably as good as can be expected in view of the small number of diffractions available and the diffuseness of all except the equatorial arcs.

The pattern is much more informative in relation to the intermolecular linking in the material.

4. Discussion.

In the foregoing paragraphs it has been supposed that the pronounced bands or lines forming the most characteristic feature of the patterns, are molecular in origin and do not arise from the crystalline lattice as a whole. The diffuse background in natural rubber was also molecular in origin

and as far as the mathematical argument is concerned the two cases are analogous except for the fact that the natural rubber showed one preferred orientation, a fact which greatly simplified the analysis of the pattern. Had the crystallites been randomly oriented about the axis of extension and the rubber pattern been a true rotation pattern the zones would have been extended along the layer lines and the pattern to be anticipated would have been very similar to that occurring for Neoprene.

There is, however, an essential difference between the two cases. For, in the natural rubber, it is supposed that the molecules are arranged in a crystalline lattice but execute thermal vibrations about their mean lattice positions. Charlesby, Finch and Wilman (1939, 1941) showed that under such conditions the expression for the intensity of diffraction in any given direction is the product of two factors, one of which defines the arc or spot interferences arising from the lattice as a whole, and the other the diffuse zones arising from the molecules. Diffuse zone patterns of this type are thus essentially associated with well-developed arc patterns. In the case of Neoprene, however, the arc patterns are extremely feeble, even when the bands are quite pronounced. We are therefore led to the conclusion that while the chloroprene molecules are

undoubtedly executing thermal vibrations, their mean positions are not necessarily those of the crystalline lattice. Thus we have in Neoprene a material in which stretching can cause uni-directional ordering of the molecules without leading to much crystallisation. Furthermore this directional ordering can in some cases be quite precise, since the bands in Figure 17a are narrow and do not show any signs of curvature.

There is, however, one strong feature of the arc pattern which is always associated with the molecular bands. This is the pair of strong equatorial arcs which have been indexed as the (200) and (120) arcs combined. Taking these into account, the most probable situation appears to be that, on stretching, considerable lengths of the chain take the direction of extension and at the same time their axial positions become fixed relative to those of their neighbours so that their lateral spacings are immediately determined, but they remain randomly arranged in the axial direction. In other words, these molecules appear to be able to slide freely over one another in the direction of their axes comparatively unhindered by links with adjacent molecules.

No such intermediate stage of ordering has been observed for natural rubber where the directional ordering appears to be always associated with the development of the

complete lattice. This difference in molecular arrangement appears to indicate a fundamental difference in the intermolecular forces in the two materials which would be expected to be reflected in the physical behaviour of the bulk polymers.

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