OPTICAL MICROSCOPE MEASUREMENT OF THE SIZE OF PARTICLES OF CARBON IN RUBBER

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Carbon black, dispersed in a transparent medium has - if the concentration and the thickness of the layer are right - the property of modifying the light passing through it in a characteristic way. If, for example, rubber and carbon black mixtures are prepared for examination according to the recommendation of H. POHLE (1), i.e. about 2% by weight carbon black in rubber, pressed out thinly between the slide and the cover glass, the intensity of colour of a carbon black can be seen by comparison, even with the naked eye by transmitted light. Looked at in this way highly active blacks look brownish grey and inactive ones bluish grey. It is very much easier to recognize definite kinds of blacks prepared in the same way under the microscope with high magnification in the bright field and it is possible to see directly fairly large particles of carbon black as well as to distinguish the colour. In this way it is possible, by comparison with standard specimens as to colour and characteristic shape of the particle, to recognize most of the carbon blacks according to kind, or at least type. In order to carry out more exact measurements of carbon particles the author has used a method using the optical miscroscope, which will be briefly explained.

The smallest object which can be recognized under the most favourable conditions with visible light measures approximately $0.2 \cdot 10^{-4} cm^3$ (2). Still smaller objects, as for example particles of a highly active carbon black, can presumably be made visible in the dark field but they cannot be measured directly.

When particles smaller than about $0.2 \cdot 10^{-4}$cm are viewed in the dark field nothing is obtained except diffraction discs. If a carbon black could be successfully prepared for the microscope so that the particles are dispersed with distances between them equal to or greater than the smallest resolvable distance, then it might be expected that every individual particle would be distinguished provided the intensity of the diffracted light is adequate. The following procedure may be adopted for the preparation of such a microscope subject.

A mixture of, for example, 2% Inca carbon black in white crepe is dissolved in benzene and a drop of the solution placed on a clean surface of water; the drop spreads out immediately, the benzene evaporates and finally there is left floating on the water a thin film of rubber with carbon black dispersed in it. This is mounted on a microscope slide and covered with Canada balsam and a cover slip. In this way the particles of carbon dispersed in the rubber can be successfully oriented in the same plane as the microscope slide.

If one of these "film preparations" is viewed in the dark field with the highest magnification each carbon granule should be recognizable by a diffraction disc as far as the intensity of light permits. According to Rayleigh's law the intensity of the diffracted light is proportional to the square of the volume of the particle under consideration assuming the shape to be spherical. By means of photographs exposed for different lengths of time it can be decided what exposure must be allowed so that even the smallest particle in such a carbon black can be reproduced. If such a series of dark field photographs is compared with the impression gained through visual observation it will be demonstrated that the eye has not registered nearly as many particles as are actually present. The amount of light diffracted from the smallest particles of a highly active carbon black, even with dark field illumination from all sides and an electric arc lamp is not sufficient to produce an impression which can be received by the eye; only the larger particles can be seen. But if a highly sensitive photographic plate is used and the correct exposure made the threshold value can be reached and even the smallest carbon particles can be identified. To avoid unduly long exposure times the author uses unfiltered arc light for these photographs; it is true that this reduces the definition of the photographs somewhat, but it makes it much easier to achieve the real object by bringing in the long wave ultra-violet radiation. Photographs in the bright field also reproduce a larger number of particles - by comparison with the visual picture - if a high contrast plate is used.

In the dark field series, Figures 1-5, the exposure times are increased four-fold for each successive picture. In Figure 1 the threshold value is only just reached by the brightest particles and as soon as the exposure time was reduced nothing was obtained. Similarly, in Figure 5 the exposure factor of the smallest, i.e. the particles of lowest light intensity, was reached in practice, and an increase in the exposure time produced no increase in the number of particles in the picture. The most important condition in the making of such a series of photographs is that the particles are dispersed widely enough, so that the unavoidable halation from the bright particles does not overlap the darker particles. The sole purpose of the present series of photographs was to show under what conditions the smallest carbon granules could be made visible and in particular what exposure time was required.

In order to measure the average volume of a carbon particle it is necessary to know the number of particles in a given space and also the space concentration in volume per cent. To discover this, the author produced, on the laboratory rolling mill, some carbon black mixtures with the purest white crepe, so that there was a known, very small carbon content. A small specimen from one of these very clean and uniformly produced mixtures was pressed out thinly between the slide and the cover slip so that the thickness of the layer was about 5 - 10μ. In a preparation like this the carbon granules do not lie all in one plane - as previously - but are disposed over the whole space and it can be assumed that they fill it uniformly. The specimen was then micro-photographed, the focal plane of the microscope being brought approximately to the region of half the thickness of the preparation. If it is certain that all the particles can be reproduced even in the bright field, particularly in the case of carbon blacks with large particles with no active components, then the photograph can be taken in the bright field. In any case of doubt the dark field photograph would certainly give equal results. Blacks which have small particles, such as, let us say, the semi-active or highly active blacks can only be photographed in the dark field.

The purpose of the photograph is to reproduce all the particles in a given zone of depth Δb by appropriate exposure times so that they appear on the photographic plate in a concentration low enough to permit satisfactory counting. To analyze such a photograph it is necessary to know the magnification, the carbon black concentration by volume per cent, and the value Δb. Every particle is counted, irrespective of the sharpness of definition of the image, provided it can be recognized as such. This process depends on the accurate measurement of Δb. In this connection it is helpful to know how far from the focal plane the carbon granules can be and still be reproduced in the photograph. A moment's reflection will show at once that all the particles cannot be evaluated alike because the smallest particles, i.e. those of lowest light intensity cannot be seen so far from the focal plane as larger ones, i.e. the brighter particles. In the first case the light intensity of the dispersion ring drops more rapidly below the exposure factor of the photographic plate - owing to the lack of focus - than in the latter case. This situation is most clearly demonstrated by an experiment using a carbon black preparation in which the particles are arranged in a plane and micro-photographed at a known inclination to the optical axis and under the same conditions as the photographic plates for the counting process.

In the case of such a photograph with carbon particles disposed in a plane and taken at a known inclination it is to be expected that, in the region of the focal zone every particle will be reproduced but that further off only the brighter ones, because here the light intensity of the small particles, being distributed over a greater dispersion ring, no longer reaches the exposure factor of the photographic plate.

The decline in definition upwards and downwards is not symmetrical as is immediately apparent from the laws of geometric optics. For analytical purposes the photograph in Figure 10 was divided up into parallel strips, corresponding to a width in the specimen of 5μ, and parallel to the focal line. The carbon particles appearing on these strips were counted and plotted graphically as shown in Figure 11.

When determining the depth Δb to be photographed with the preparation placed at an angle, it is assumed that the number of particles actually present in each strip-width is, on the average, the same and also equal to the number obtained for the strip in which the definition is greatest (Figure 10 - strip No. 4, number of particles 150). The drop in the number of particles to the left and right is thus due only to the increasing lack of definition in the photograph. As, unfortunately, it was not possible to continue the photograph until the declining particle-count reached zero, the missing values were obtained by graphic extrapolation (Figure 11). There is, thus, a reconstruction of the total of all the particles which would appear if the photograph in Figure 12 is imagined to be extended to the left and the right and this sum 1055 is divided by the average number of particles in each strip 150. The result, 7, indicates that, on the whole, there are as many particles reproduced as there are in 7 strips. In other words the same result is obtained by counting all the particles which are reproduced, taking into account the increasing lack of definition, and by counting all the particles in 7 strips. Thus we shall not go wrong if, when considering a series of photographic counting plates (Figure12-16), we put the total number of particles counted equal to that number of particles actually found to exist in a space whose depth is, as shown in Figure 10, the difference in depth of 7 strips. This difference can be calculated from the known inclination

a:b = 1.34:21.5 (Figures 9 and 10) giving $2.2 \cdot 10^{-4}$ cm. This would yield a value for the length Δb which would make possible the calculation of the average particle volume on the basis of the photographic plate count.

The photographs 12-17 show photographs with an increasing carbon content. It appears from these that the rubber material in which the black is dispersed itself contains foreigh bodies so that the number of the particles photographed with a zero carbon concentration does not drop to zero. With a few deviations there appears to be a linear relation between the number of particles counted and the concentration - illustrated in Figure 18 - always keeping within the range of small carbon concentrations. It is self-evident that when evaluating photographic count-plates the zero value must be deducted.

The photograph shown in Figure 17, with a concentration of 0.1% carbon black Inca in crepe, is not suitable for a quantitative determination of particle sizes because the concentration is far too high and it would be quite impossible to count all the particles owing to the accumulations which they form.

The actual evaluation is performed quite simply according to the formula -

$$Vm = \frac{F \cdot \Delta b \cdot Vol.\%}{100 \cdot n}$$

where Vm is the average particle volume

Δb is the depth of the photograph as described above

Vol.% is the % volume of carbon in the whole mixture

n is the number of carbon particles counted in the photographed surface F.

Example: (evaluation of Figure 16)

$$F = 1215 \cdot 10^{-8} cm^2$$
$$\Delta b = 2.2 \cdot 10^{-4} cm$$
$$Vol.\% = 3.09 \cdot 10^{-5}$$ (corresponds to 0.006 weight % in rubber)
$$n = 102$$ (Figure 16 shows 156 particles minus the 54 particles counted in Figure 12 under the same conditions without carbon black)
$$Vm = 8.10^{-16} cm^3$$

This result is based on the dispersion of carbon black in rubber and it will be understood that such a number can only be obtained for the particle volume which would correspond to an optically perceptible dispersion in the rubber. Hence, if there should be, in the rubber, particles of carbon formed, perhaps, by the conglomeration of single particles at one spot - smaller than the resolving limit of the microscope - a result must be expected which corresponds to the volume of the conglomeration as a whole rather than the particle volume. Another important factor is the concentration of the carbon-rubber mixture. If this is too high the points of light which have to be counted lie too close together so that the unavoidable halations of the larger particles make an accurate count impossible (Example Figure 17). It must also be noticed that in addition to the light from the particles which can be counted, light will be diffracted into the objective from particles lying above and below those actually to be reproduced. This stray light causes the dark field to become brighter with the result that the particles of low light intensity no longer stand out from the background, with sufficient clarity. It must therefore be expected that if there is too high a concentration of carbon false results will be obtained indicating too great a volume, because all the particles will not have been included in the count. The author's experience shows that good results can always be expected if the concentration is such that in a well maintained dark field there are no more than 500 particles in an area of approximately $2000 \cdot 10^{-8} cm^2$ and a depth of Δb(magnification 2000 : 1). On the other hand it is not advisable to have fewer than 100 particles in this same space because this would affect the desired average value of probabilities of particle accumulation to too great an extent. There is doubtless a personal factor involved in the counting of the photographs, but this would be partly compensated by the fact that the same person would be measuring the value of the depth Δb by counting. Another inaccuracy arises from the extrapolation (Figure 11) which, however, remains within narrow limits in relation to the total result because the decisive factor in calculation is the centre of the picture which has actually been observed and the extrapolation is confined to the edges where the numerical significance is slighter. It should also be mentioned that the adjustment of the microscope must be uniform, particularly in the case of the dark field. After considering all these factors the author thinks that errors due to procedure should not cause deviations of more than 50% in the final result. In the large majority of cases the results were contained within much narrower limits. At all events errors arising from procedure are small by comparison with the differences caused by differing levels of activity of the carbon blacks so that this can still be regarded as a successful method for the characterization of the technically interesting carbon-containing rubbers.

It will be particularly interesting now to compare the results of measurement made by the above procedure with those based on electron-optical measurements and photographs. It must be borne in mind while doing so that, on the basis of statistical measurements, the procedure here described gives the average volume of the particles and gives no information about the shape of the particle. Electron-optical methods on the other hand, yield highly magnified "silhouettes" of the carbon particles from which much can be learnt about the shape - but less about the volume - of the particles. There is a difficulty in connection with the electron-optical photographs in that the results do not indicate the numerical relation which the particles bear to each other and, as they show fairly large differences in size it is difficult to gain a picture of the average size. In order to obtain some guidance on this the author measured the carbon particles shown in electron photographs and converted them into volumes of the smallest and largest particles, using the method indicated. The results are given in Table I.

Comparison of the photo-optical results with those from the electron pictures (as described in the previous paragraph) shows a good measure of conformity in the case of the carbon black CK 4. It is important to note here that this carbon consists entirely of a highly active component - as is apparent from observation by photo-optics in the bright field. This is not quite the case for the black P 1250. There is no doubt that this carbon black consists mainly of particles corresponding to the electron photographs quoted. But it also contains other, larger particles - as can be clearly seen, even with the bright field illumination of the photo-optical microscope - which, obviously present to a smaller extent, could not be seen with the electron photographs. With the statistical measurement of the procedure described it can be understood, therefore, that the particle-volume measured photo-optically is a little higher than would be expected from the electron photograph. On the other hand, in the case of Inca black, the electron photograph also consists of two distinct components, differing considerably from each other, and it is very difficult to gain any idea of the average volume of the particles from the electron picture alone. Considered purely from the aspect of rubber technology the photo-optical result seems satisfactory, even when compared with the other carbon blacks. With Luv 36, however, there is quite definitely a disparity between the results from the two procedures. The smaller particles reproduced in the electron picture, considered as spheres, agree with the photo-optical values, but the larger particles exceed them by a considerable amount. It is not possible here to answer the question whether perhaps the black under investigation was not quite the same in both cases or whether the shape is not spherical. All that need be said is that the photo-optical result is satisfactory inasmuch as it conforms well with the impression obtained by observing this carbon black under the optical microscope in the bright field, particularly by comparison with P 1250 and "Elastic". In the case of flame-carbon black "Elastic" there is reasonable agreement between the results from both procedures provided the particles which cannot possibly be regarded as spherical are thought of as cylinders or as a coherent, elongated aggregation of spheres (similar to the inactive component of Inca black). They are then of an order of magnitude which can be directly resolved to some extent with the optical microscope the same impression of the shape is then obtained as in the case of the electron photograph already mentioned.

SUMMARY

A process is described which makes possible the measurements of commercial rubber carbon blacks by means of the optical microscope and gives the average volume of the carbon particles. The process provides for the photographing of the carbon particles dispersed in the rubber at high magnification on a dark ground and for counting from the photographic plate. The thickness of the photographed section is ascertained separately by photographing at an angle a preparation with particles of the same carbon black dispersed in one plane. The average volume of the particles was then calculated from the thickness, the surface count and the concentration by applying the usual ultra-microscopic formula.

TABLE I.

Type of carbon black	Average Volume Vm photo-optic	Dimensions of particles (3) (electron-optically)	Volume calculated on basis of electron-optical measurements.
CK 4	0.3×10^{-16} cm³	2.5×10^{-6} cm diameter of smallest particles 5.0×10^{-6} cm diameter of largest particles	Spherical shape 0.08×10^{-16} cm³ for smallest particles 0.65×10^{-16} cm³ for largest particles
P 1250	5.10^{-16} cm³	5.7×10^{-6} cm diameter of smallest particles 10.0×10^{-6} cm diameter largest particles	Spherical shape 0.97×10^{-16} cm³ for smallest particles 5.25×10^{-16} cm³ for largest particles
Inca	8.10^{-16} cm³	Active component: 1.5×10^{-6} cm diameter of smallest particles 7.0×10^{-6} cm diameter of largest particles	Active component: Spherical shape 0.018×10^{-16} cm³ for smallest particles 1.0×10^{-16} cm³ for largest particles
		Inactive component: elongated form 80×10^{-6} cm length 10×10^{-6} cm width	Inactive component: As cylinder 140×10^{-16} cm³ or as elongated, coherent aggregation of spheres with single spheres of 17×10^{-16} cm³ 100 to 150×10^{-16} cm³
Luv 36	23×10^{-16} cm³	10×10^{-6} cm diameter of smallest particles 40×10^{-6} cm diameter of largest particles	Spherical shape 5.10^{-16} cm³ for smallest particles 335×10^{-16} cm³ for largest particles
Elastic	126×10^{-16} cm³	Elongated form 66×10^{-6} cm length 16×10^{-6} cm width	As cylinder 170×10^{-16} cm³ or as elongated, aggregation of spheres 100 to 200×10^{-16} cm³

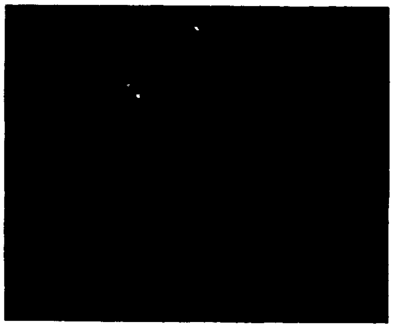

Fig.1

Fig.2

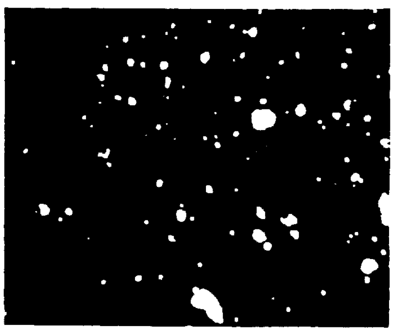

Fig.3

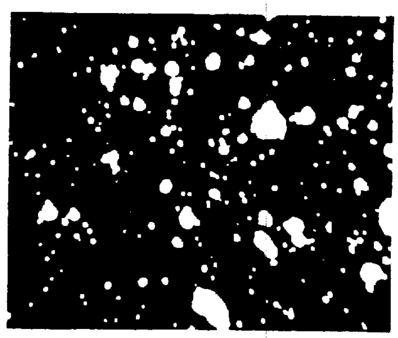

Fig.4

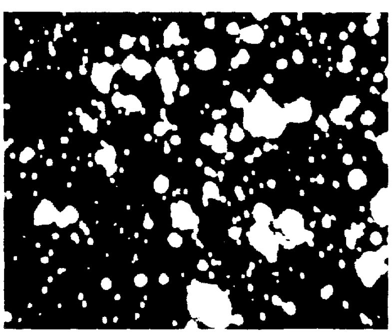

Fig.5

Fig.6

Figs.1-6: The photographs show the same area of a prepared film of rubber containing 'Inca' carbon black. All the carbon black particles are located in the objective plane. Magnification 2000:1. Objective, 1/12 Leitz Fluorite, Ocular, Periplan 10x, Extension 46.5 cm. Arc lamp without filter. Leitz dark field condenser D 1.20. Figs. 1-5 Agfa Isochrome plate, Fig.6 Monlalamp 5 amp. Leitz 2 stop condenser, Aperture stop fully open, Green filter, Perutz silver eosin plate. Exposures Figure 1, 2 seconds, Figure 2, 8 seconds, Figure 3, 32 seconds, Figure 4, 128 seconds, Figure 5, 512 seconds, Figure 6, 15 seconds. The magnification given is for the original negative.

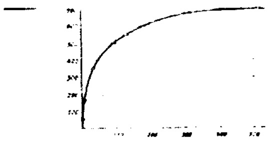

Fig.7: Graph illustrating the number of particles reproduced in relation to the exposure time. Inca black, dark ground series (Figs.1-5)

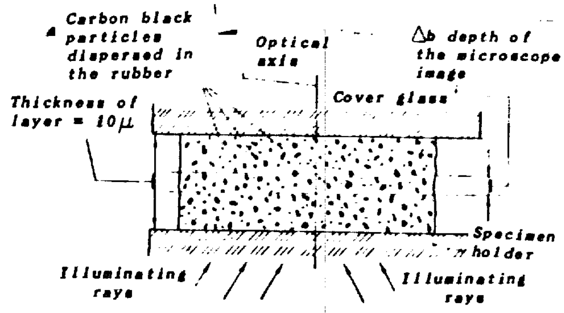

Fig.8: Section illustrating the arrangement for taking a photograph for counting

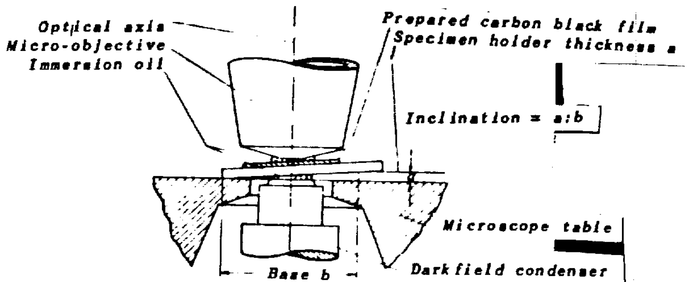

Fig.9: Section illustrating the method of tilting the prepared film in order to determine the depth of the microscope image

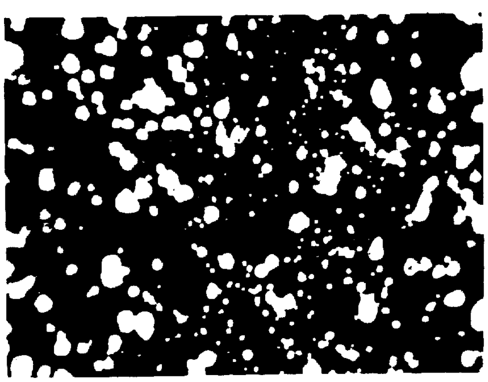

Fig.10: Plane film prepared for Inca carbon black at a known inclination. Objective, ocular as in Figs. 1-6, Inclination a:b - 1.34:21.5, Agfa Isochrome plate, exposure 8 minutes. Magnification 2000:1.

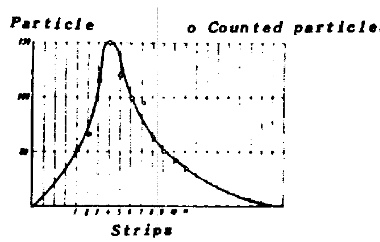

Fig.11: Graphic evaluation of Figure 10 showing the number of particles with respect to successive strips. The curve is extrapolated both to the right and the left beyond the limits of the photograph.

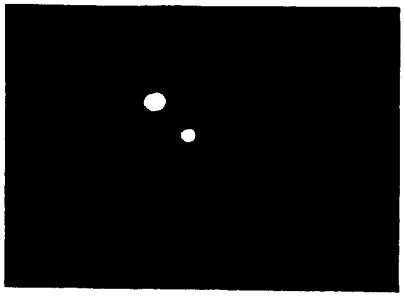

Fig.12: Counting plate for white crepe without carbon black. Counted particles 50.

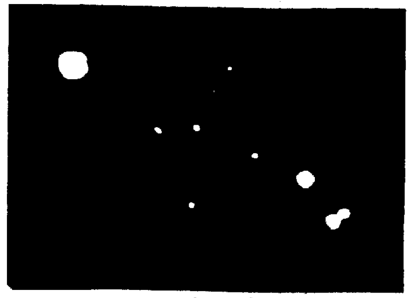

Fig.13: Counting plate for white crepe with 0.001% Inca carbon black. Counted particles 75.

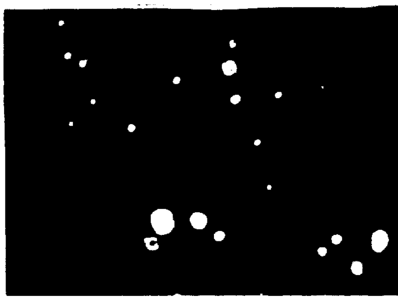

Fig.14: Counting plate for white crepe with 0.002% Inca carbon black. Counted particles 67.

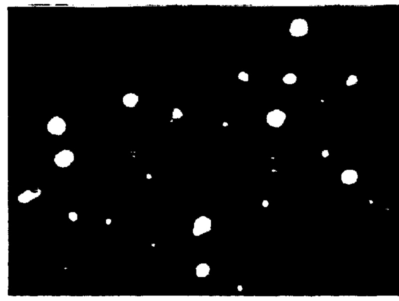

Fig.15: Counting plate for white crepe with 0.004% Inca carbon black. Counted particles 124.

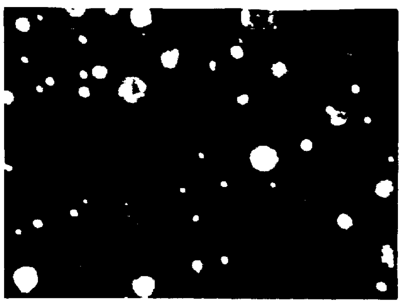

Fig.16: Counting plate for white crepe with 0.006% Inca carbon black. Counted particles 156.

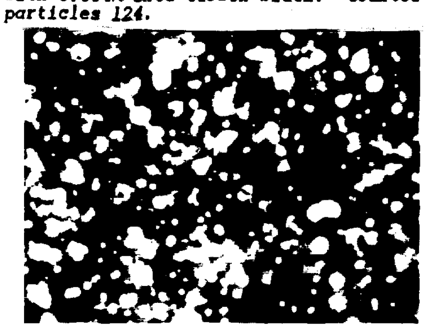

Fig.17: Counting plate for white crepe with 0.1% Inca carbon black.

Figs.12-17: Microscope data. Exposure and plate material as for Figure 5. The carbon black concentrations given indicate that in each case the given percentage of carbon black in grams was added to 100 grams of rubber. Counting was done from the plate. It is to be expected that the large number of weak light spots will not show up in the reproduction.

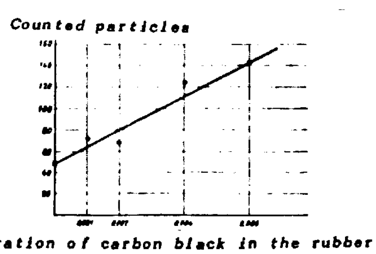

Fig.18