

Recent Development in the Art of Rubber Microsectioning¹

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There has lately appeared an article² by Messrs. Depew and Ruby in which the authors point out the desirability of studying the nature and dispersion of compounded pigments in rubber microsections.

Their method of preparing the sample for sectioning, by freezing with carbon dioxide and liquid air, entails certain disadvantages which are difficult or quite impossible to overcome. Chief among these are the annoyances encountered in obtaining, transporting, and keeping liquid air.

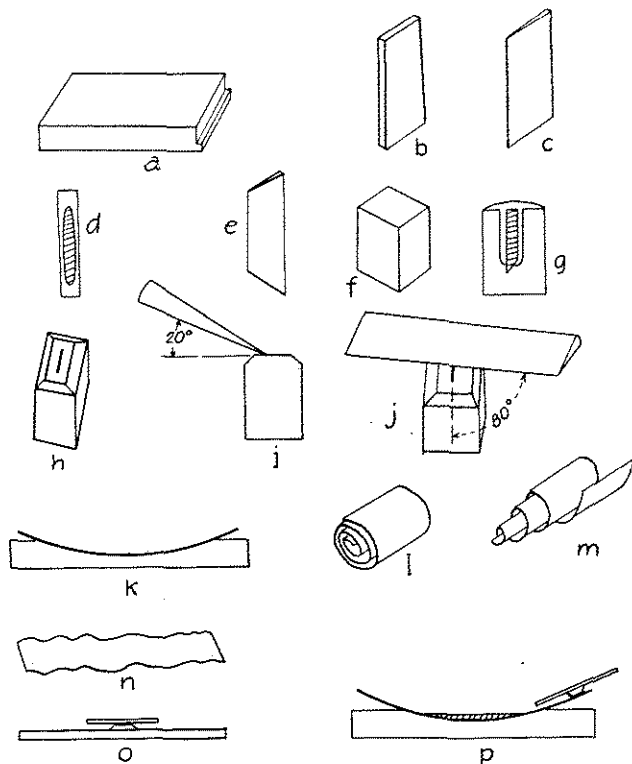


FIG. 1

In addition, the method usually necessitates the use of large amounts of carbon dioxide, before a satisfactory section can be secured. The main drawback is met in the comparatively high temperature of the knife. As the blade passes over the specimen, the heat it (the blade) contains is partly transferred to the frozen rubber causing it to thaw, with a consequent change in volume, thus making it impossible to regulate the thickness of section. This fact is particularly objectionable when it is desired to obtain the thin sections required for the examination of rubber containing high percentages of gas black. Briefly, the method fails economically, both in respect to expense and time.

After stating the objections to the freezing method it would hardly be fair to omit emphasizing its chief virtue, *i. e.*, the fact that the specimen is not chemically prepared, and therefore a possibility of destroying the rubber structure or influencing the dispersion of the pigment is eliminated. For this reason, alone, it is not desirable to abandon entirely the idea of employing the freezing method at times.

¹ Presented before the Division of Rubber Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

² "Some Microsections Cut from Vulcanized Rubber Articles," *THIS JOURNAL*, 12 (1920), 1156.

THE NEW METHOD

This method is purely a chemical one. The elasticity of the rubber is destroyed and a proper rigidity acquired by revulcanization with a very dilute carbon tetrachloride solution of sulfur chloride.

It is essential that the specimen be of proper size and shape for sectioning. From a block of the rubber to be examined, (*a*, Fig. 1) either a rectangular or wedge-shaped corner is cut (*b* and *c*), approximately $0.5 \times 4 \times 20$ mm. in size. This piece is placed in the vulcanizing solution (the strength of which is discussed below) and treated for a length of time that will vary according to the nature of the rubber, thickness of the section, and, of course, the concentration of the solution. At stated intervals, the specimen is removed and examined by slicing off a small portion of the end and testing the hardness with a needle point.

The ability to recognize the proper degree of hardness is easily acquired with practice; to attempt to describe it is difficult. As a rule there should be no indication of elastic recovery where the rubber has been scratched or depressed. Above all there should be no soft unvulcanized core, as shown at *d*. On the other hand, the specimen must not be so hard that it cracks and crumbles upon cutting, but rather it should slice as easily as a piece of soft wood in the direction of grain.

Assuming that the specimen is correctly vulcanized, the next step is to allow it to become thoroughly dry (preferably by vacuum treatment) and then to sharpen it at one end, as at *e*, simply for convenience in inserting it in the paraffin mounting block. This block, *f*, is rectangular in shape and roughly $15 \times 15 \times 30$ mm. It is clamped in a vise and a hot nail or other convenient instrument pushed into its upper end to a depth of about 18 mm., to produce a cavity in which the specimen is placed.

The pointed end *e* must be pressed firmly into the paraffin and the face of the block covered with a few drops of melted paraffin (Fig. 1, *g*). After cooling, the block is trimmed as shown at *h*. It is then ready to be sectioned.

The knife must be of the flat-faced type and make a vertical angle with the specimen of about 20° and a horizontal angle of approximately 80° (Fig. 1, *i* and *j*). Not less than ten sections should be cut at a time. They will adhere to form a ribbon which is easily removed to a watch glass, *k*. A small hand glass is employed to count the number of sections imbedded in the ribbon in order to note whether the microtome has "skipped" or not. In case it has, it is then impossible to ascertain the thickness of the section from the microtome setting.

The paraffin adhering to the microsection is now removed with a few cc. of toluene. The specimens, upon examination,

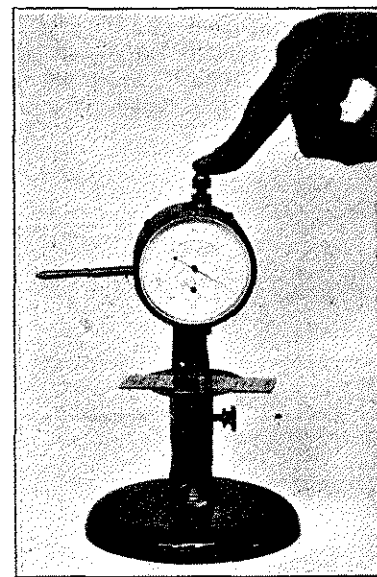


FIG. 2

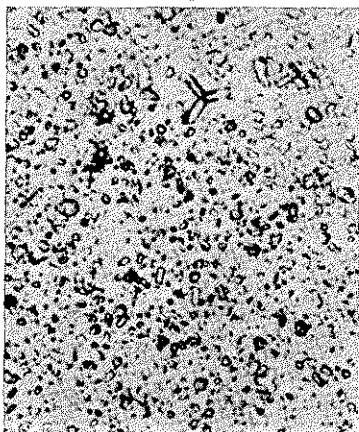


FIG. 3

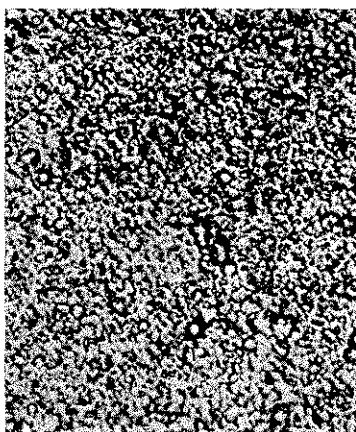


FIG. 4

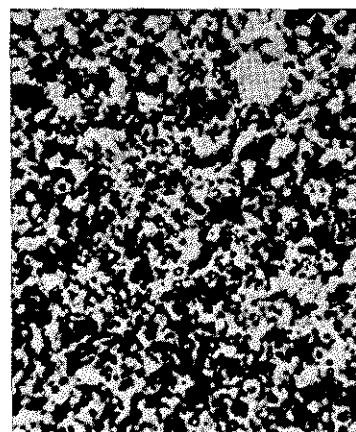


FIG. 5

will be found to be curled either in the manner shown at *l* or at *m*. If the former is the case, they will be difficult to uncurl and the horizontal angle of the knife must be made more acute so as to prevent this form of curling. Next the sections are removed from the toluene by sliding them up to the edge of the glass with the aid of the needle.

If the sections are thick ($3-5\mu$) they will probably become detached from the glass upon drying and are easily transferred to the microscope slide. The mounting medium is piperine (never Canada balsam).¹ A few small crystal fragments of this material are placed on the slide and warmed till melted. Upon cooling, piperine will remain plastic and sticky for some time. While in this condition, the section is placed on its surface and covered with a glass (Fig. 1, *n*). Upon alternately warming and pressing on the cover glass the excess of piperine is gradually squeezed out.

The specimen is next examined with a low power microscope. If it is found to be badly wrinkled, as shown at *o*, or to contain objectionable air bubbles, the slide is transferred to a hot plate and heated for a minute or so till the piperine is quite fluid. While in this state it is necessary to apply a comparatively high pressure in order to remove the air bubbles and at the same time to flatten the section as much as possible. The author has found a thickness gage convenient for this purpose. The slide is placed on the stage and pressure applied with the finger on the upper end of the plunger (Fig. 2). After cooling, the mount is ready to be labeled and examined.

If the section is quite thin ($0.5-1.5\mu$) it will not become detached from the watch glass upon drying. In such a case it is sometimes possible to detach it with the needle point. If this fails it is necessary to resort to the following method: First melt the piperine on the microscope cover glass, instead of the slide. Invert it so that the drop will hang downward. Upon solidification press the drop against the section, as shown at *p*, Fig. 1. The specimen may become slightly damaged by this process but it will adhere to the piperine and can now be mounted by the method previously described.

Reference has been made to the strength of the vulcanizing solution. This will vary with the kind of rubber to be treated. A zinc oxide tread, for instance, can be sufficiently prepared in 5 to 10 min. in a carbon bisulfide (N. B., not carbon tetrachloride) solution which contains just enough SCl to impart to it an easily discernible yellow tint, perhaps several drops in 50 cc. of solution. If this is found to be too weak the strength may be increased or the specimen sliced thinner. The best concentration is in all cases quickly and easily found by trial.

¹ In a rubber section mounted in balsam, zinc oxide becomes quite invisible, excepting the largest particles, which are always readily seen.

In preparing rubber which is compounded with gas black, the solution should be made with CCl_4 , as otherwise brittleness is liable to ensue. Carbon tetrachloride solution acts much more slowly and consequently should be made stronger—15 drops to 50 cc. In some cases it is necessary to allow treatment to continue from 1 to 3 hrs. before the specimen is hardened completely. Any number of samples, however, can be prepared together so that the time lost is not a serious factor.

SOME RESULTS OBTAINED WITH THE SCl METHOD

A rubber microsection made as described will be approximately 0.5×4.0 mm. in area. On account of the minute size of the compounded pigment particles it has been found most convenient to employ for examination a magnification of at least 1500 diameters.

While a microsection of this size may seem rather small to show all the characteristics that a particular rubber sample possesses, in reality it will be found amply large enough. If the field of the microscope were so extended that it could give a single view of the entire section it would appear (at 1500 diam.) to be a strip, in round numbers, 3 ft. by 20 ft. in area.

Sections prepared by the sulfur chloride method possess beautiful transparency and uniformity in thickness. They are practically ideal for visual examination where it is always possible, by varying the fine adjustment, to bring any part of the mount (and at any depth) into focus, hence the slight lack of flatness, which these sections often have, is not objectionable.

A section which is not perfectly flat is a difficult one to handle from a photomicrographic viewpoint; however, most specimens contain areas that are sufficiently free from this defect so as to enable one to obtain fairly satisfactory photomicrographs.

Fig. 3 is a zinc oxide tread. No difficulty is experienced in obtaining good sections of rubber compounded with normal amounts of this material. On account of its transparency these sections may be cut quite thick ($3-5\mu$).

Fig. 4 is a specially prepared sample containing 100 volumes of rubber to 100 volumes of zinc oxide. Even with this high percentage of oxide the pigment particles are uniformly distributed, showing absence of aggregation. The section was not difficult to make.

No photomicrograph can do justice to the sections presented in Figs. 5 and 6. The former shows lampblack, always existing in rubber flocculated into small groups with clear water-white spaces between. The individual particles are not discernible as they are never found dispersed. A great deal of the detail in this section cannot be seen in the

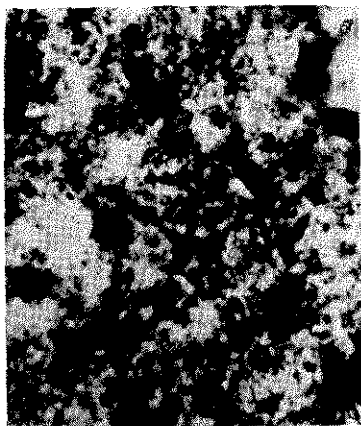


FIG. 6

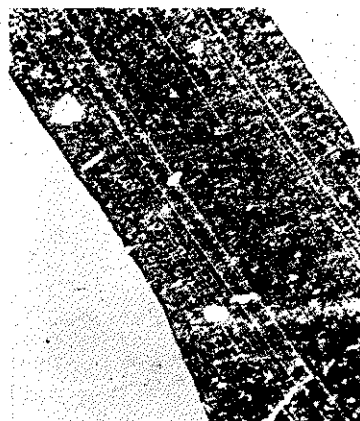


FIG. 7

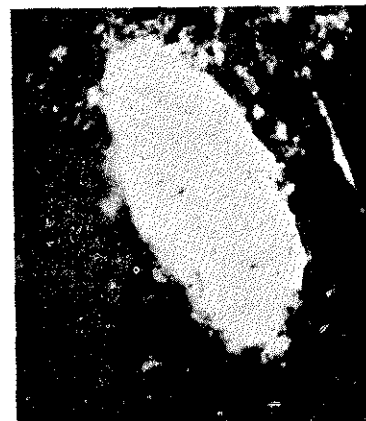


FIG. 8

photomicrograph. Fig. 6 is rubber compounded with gas black. This black is found much better distributed than the former, though one inexperienced in work of this nature might easily infer otherwise from a comparison of the photomicrographs. Here again (in Fig. 6) much of the detail observable with visual examination is lost in the attempt to reproduce it photomicrographically. As a matter of fact, a more difficult subject than rubber containing normal amounts of gas black cannot be found in the entire field of photomicroscopy. There is no difficulty whatever in readily distinguishing between a rubber compounded with lamp-black and another containing gas black, upon microscopic examination.

Fig. 7 shows a tread containing gas black and clay. The magnification is but 67.5 diameters. The clay is best ex-

paraffin in which the rubber is soaked before sectioning. The sample was not treated with sulfur dioxide, no pigment being present to interfere with the transparency, hence a thick section (100-200 μ) could be used. The paraffin itself will produce sufficient rigidity to make possible the cutting of these abnormally thick sections.

The microsection was next washed with toluene to remove the paraffin and then dried and mounted in glycerol. If such a mount is examined immediately it will be found that the para toner has crystallized and if the process of crystallization is to be studied, solution must first be obtained by warming the slide. The rubber will act as a liquid solvent and cause complete solution of the toner. When recrystallization commences it can be studied microscopically, using a low power objective. The material sends out branches

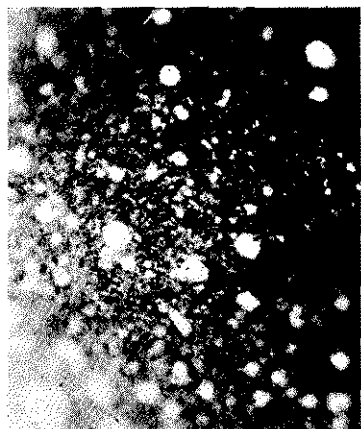


FIG. 9

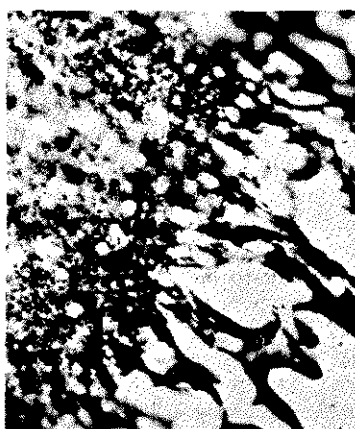


FIG. 10



FIG. 11

amined between crossed nicols where it shows extinction and interference colors. Fig. 8 is the same sample magnified 1500 diameters in order to observe the gas black, individual particles of which can be seen along the edge of the clay particle.

Frequently, rubber compounded with gas black will be found to contain innumerable pocket-like spaces absolutely devoid of pigment particles. Fig. 9 shows a section of this kind. So far it has been impossible to determine whether these spaces are empty or contain a substance which the gas black particles are unable to penetrate. Fig. 10 is a rough torn edge of a similar section showing a sponge-like structure, due to these pockets.

Growth of crystalline substance in rubber is an interesting procedure to study. Fig. 11 is a section containing crystallized para toner. This substance is first dissolved in melted

apparently with perfect freedom just as though it were suspended in a liquid medium instead of a solid one.

In conclusion the author wishes to state that he has constantly borne in mind, while preparing rubber microsections by the sulfur chloride method, that the rubber is given a chemical treatment that might possibly produce effects not present in the untreated original specimen. In order to ascertain if undesirable alterations had appeared it was necessary to make comparisons with specimens prepared by the freezing method. Wherever it was possible to do this the results given by the two methods were found to be identical.

ACKNOWLEDGMENT

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