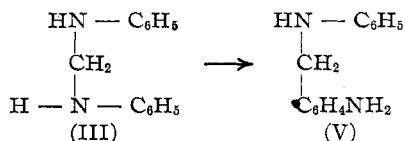
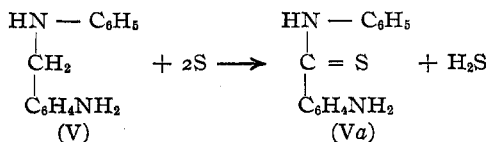


Form IVa very closely resembles thiocarbanilide and is probably one of the reaction products which is formed from methylene-diphenyl-diamine when this compound is used as an accelerator for the vulcanization of rubber.

(c) Methylene-diphenyl-diamine in the presence of aniline, either added as such or formed by Reaction b, undergoes a semidine transformation with the aniline.



This reaction takes place at temperatures even lower than milling temperatures. Paramido-benzyl-aniline (V) is a liquid which is crystallizable with difficulty and forms easily from (III), there being no difference in the curing power of the two compounds. Form V reacts easily with sulfur to produce paramido-thiobenzenilide.



Form Va is another compound very similar to thiocarbanilide, to which may be attributed a portion of the curing power of the original accelerator.

The main reaction of this type of methylene accelerators is evidently to substitute thiocarbonyl groups for methylene groups. This produces compounds very similar to thiocarbanilide and which may be considered as being derived from thiocarbanilide by similar condensation and semidine reactions, although we have been unable to prepare them directly from thiocarbanilide.

In the interaction of hexamethylene-tetramine with sulfur during the cure, we have another possibility of the formation of carbon bisulfide reaction products with amines. Hexamethylene-tetramine reacts very readily with sulfur at curing temperatures, producing a multitude of products including hydrogen sulfide, ammonia and carbon bisulfide in large amounts. Dubosc<sup>1</sup> has described the sulfur reaction products of hexamethylene-tetramine, but for some unaccountable reason has absolutely overlooked two of the main reaction products, ammonia and carbon bisulfide. The accelerating action of hexamethylene-tetramine may therefore be explained by the interaction of this ammonia and carbon bisulfide to form a dithiocarbamate. This allows us to classify hexamethylene-tetramine as a thiourea accelerator.

With a large majority of accelerators there is no possibility of the formation of thiourea derivatives by a reaction with sulfur. As far as is known, all accelerators containing methylene groups, similar to those described, react easily with sulfur at curing temperatures to produce thiourea derivatives. This does not include, however, the methylene groups of such

compounds as piperidine, or pentamethylene-diamine which on heating loses ammonia and forms piperidine.

#### SUMMARY

I—Organic accelerators containing methylene groups, similar to those described, readily react with sulfur to produce thiourea derivatives.

II—These sulfur reactions take place at curing temperatures and may throw some light on the mechanism of the reactions of these accelerators during vulcanization.

#### VOLUME INCREASE OF COMPOUNDED RUBBER UNDER STRAIN<sup>1</sup>

By H. F. Schippel

AMES HOLDEN MCCREARY, LTD., MONTREAL, QUEBEC, CANADA

Received October 6, 1919

The first record of this interesting phenomenon of volume increase in rubber under strain dates back as far as 1884, when Joule recorded the fact that the specific gravity of rubber decreased upon stretching it. His test results stated a change of specific gravity of 0.15 per cent for a 100 per cent stretch. This is a very small increase, and therefore his experiments were made upon comparatively pure rubber, unmixed with pigments, as the present paper will show.

In 1889 Mallock made tests upon pigmented rubbers of different kinds, but he made the volume elasticity tests upon the samples only by applying pressure to the water in which he immersed them, thereby simply corroborating the results of the previous investigator.

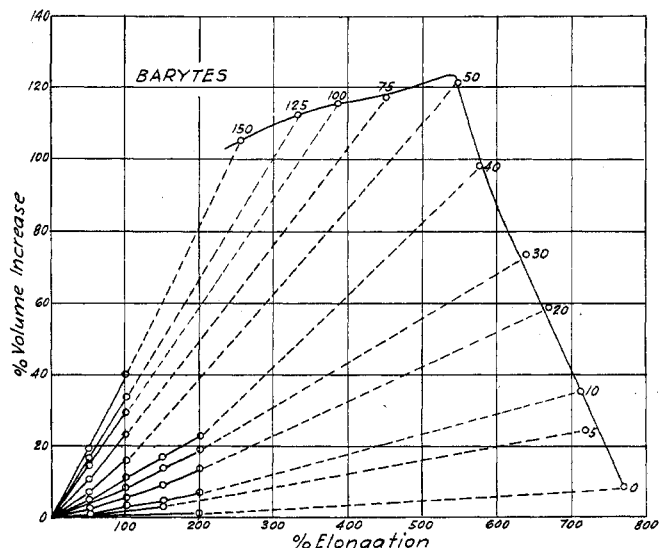


FIG. I

Again, in 1890, Sir William Thomson stated that a column of rubber when stretched out suffers no sensible change in volume, and that the contraction of any transverse diameter must be sensibly equal to  $\frac{1}{2}$  of the longitudinal extension, and rubber may therefore be regarded as an incompressible elastic solid. This is also true of pure rubber.

<sup>1</sup> Presented before the Rubber Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 4, 1919.

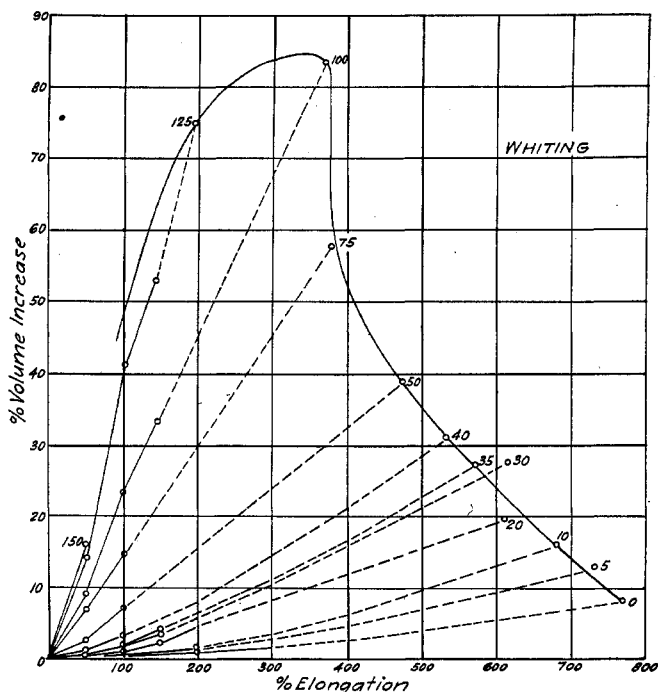


FIG. II

While studying the nature of the stress-strain curves for rubber containing different pigments in varying quantities, the writer considered the stability of the rubber surrounding each particle of pigment in the rubber body, and thought that possibly when the rubber body was elongated sufficiently the rubber might pull away from the particles of pigment in their axes of stress and cause vacua to be formed on both sides of each particle, the net result of which would be a considerable increase in the volume of the rubber body as a whole.

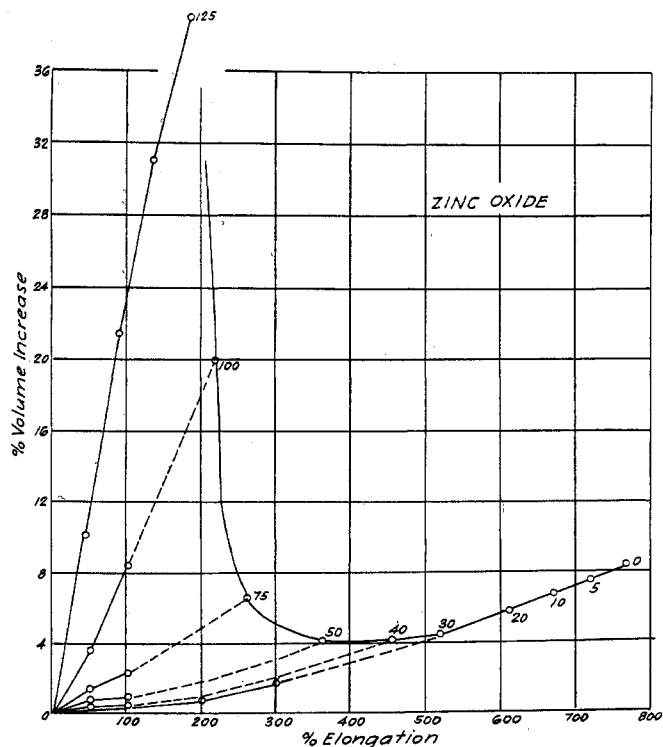


FIG. III

A preliminary test was made by preparing a transparent vulcanized compound containing a fair proportion of medium-sized lead shot. When this compound was stretched, the formation of vacua proceeded gradually until each lead shot had its conical vacua on both sides in the direction of strain. This was very satisfactory and the test was immediately applied to miscellaneous samples of rubber compounds, with the result that this integral phenomenon was actually found to take place. It was more noticeable in the red rubber than in the white. Also, after keeping the samples under tension for some time and then releasing them, temporary increases of volume were noted, which were due to sub-permanent set, or the diffusion of gases into the vacua, or both. In certain cases the observed volume increases under simple strain were remarkable. For example, a specimen made up of 100 g. fine Para, 30 g. litharge, 5 g. sulfur, and 337 g. of whiting, and press cured for 30 min. at 40 lbs. steam pressure, gave a volume increase of 52 per cent at an elongation of 140 per cent, while the estimated volume increase for a similar compound containing 215 g. barytes in place of the whiting was 120 per cent at the breaking point. In the former

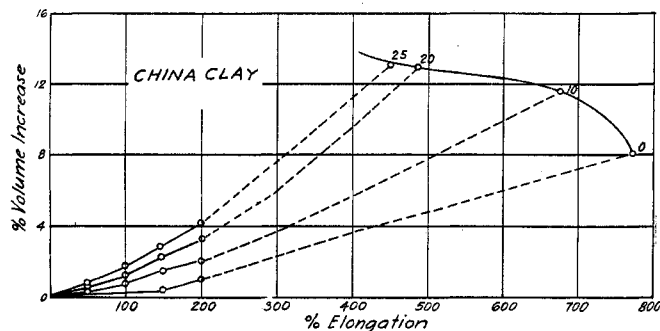


FIG. IV

case, the average value of Poisson's ratio up to the breaking point was 0.39 and in the latter case 0.31. These values are not at all abnormal, but their cumulative effect in a substance which has the ability to withstand comparatively enormous elastic strains is worthy of serious consideration from a physical standpoint.

For smaller percentages by volume of barytes, the volume increase was found to be less at the breaking point, and similarly for larger volume percentages, due in the latter case to the formation of local contractions corresponding to that of metals.

It was also noted that when barytes was substituted by an equal volume of lampblack the volume increases for any given elongation were smaller.

Systematic tests were accordingly made upon a series of compounds containing in various volume percentages one of the following pigments in each case: barytes, whiting, zinc oxide, china clay, red oxide, lampblack, and carbon black. The curves give graphically the results obtained.

The common base was made up of 100 parts by weight of fine Para, 5 parts sulfur, and 30 parts litharge, the weight of the test pigment added in any case being

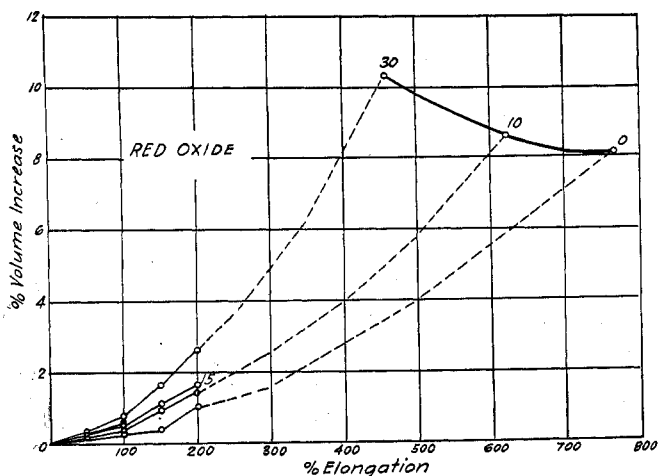


FIG. V

the volume index for that case multiplied by the specific gravity of the pigment.

A blank test was made by stretching the base only without any other pigment content. The curve obtained is marked "O" on each series of curves for the pigments.

#### METHOD OF PROCEDURE

Test rings, having a cross-sectional diameter of  $\frac{1}{2}$  in., and an outside diameter of  $2\frac{1}{4}$  in., were made from each compound up to about 35 volumes content. For volumes above this, the compounds were too stiff to make a perfect fit in the ring mold, and flat slabs about 100 mils thick were made, from which flat rings were cut. The internal circumference of the rings was approximately 4 in. Each ring was stretched consecutively over each of a graduated series of steel bars from 3 to 8 in. long, or as far as the ultimate stretch of the rubber would allow, and the volume increase was calculated by determining the change of specific gravity. This method, which avoided the construction of any special apparatus, and was very accurate, was the suggestion of Mr. W. B. Wiegand, whose inspiring coöperation in this and other rubber researches the writer takes pleasure in acknowledging.

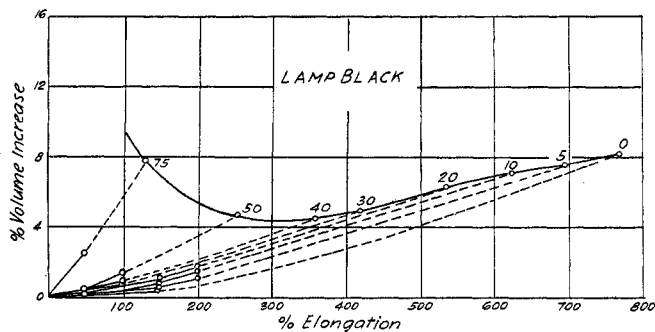


FIG. VI

(F) BARYTES—The test results are shown by that part of each curve in full line. It was found impossible to obtain higher elongations than 200 per cent for the large rings, owing to their failure by slow tearing when stretched above this value. The curves approximate closely to straight lines, showing that the volume increase varies almost directly with the elonga-

tion. Also, for a constant elongation, the volume increase progresses with the percentage of barytes in a roughly proportionate manner. There appears to be no adhesion whatever (or very little) between the rubber and the particles of barytes, because there is a volume increase in the compound containing only 5 volumes of barytes. The particles are certainly not crowded in a 5 per cent mix, and their surfaces do not necessarily transmit the whole local stress, but on account of this early separation of the pigment particles from the rubber, the particles take no important part in the stress-strain curve for the body, since the stress is transmitted through the rubber only.

It was thought that possibly the large volume increases might be due to the pigment entering the rubber in agglomerated masses, and that most of the increase in volume might be due to ready separation of particles which were in dry contact. Accordingly, two tests were made to determine this, one test of a sample of compound milled for 60 min. instead of 21 min. for the normal mix, and another test upon a sample which was softened to cement consistency in gasoline, thoroughly mixed, dried, and press-cured as usual. The excessively milled sample showed a very slight decrease of percentage volume increase, but the decrease of this property in the cement

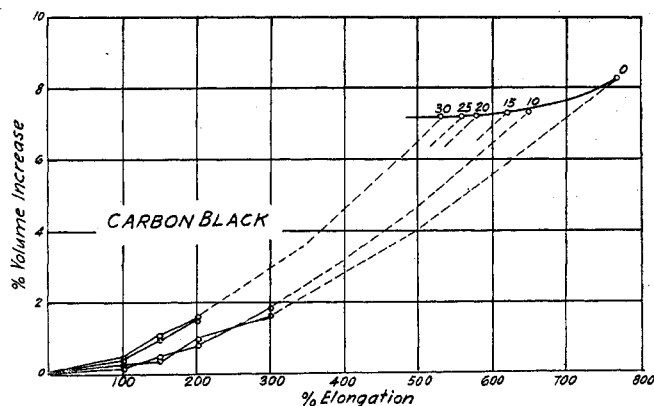


FIG. VII

sample was more considerable. The entry of the gasoline into the compound presumably softened the rubber and allowed it to flow around each particle, wetting the whole mass of pigment thoroughly; so that, although part of the volume increase under stretch is due to the separation of pigment surfaces in dry contact, the larger part of the increase is due to rubber separation from the surface of the particles.

The curves were extended as shown by the dotted lines to the point corresponding to the ultimate percentage elongation as obtained from standard breaking tests on a tensile testing machine. The full-line curve joining these points is of special interest. The discontinuity above 50 volumes is due to the formation of local contractions in the test ring, so that the whole body of rubber does not receive the same proportional elongation. The neck is similar to that formed on metal specimens. By mechanically working the rubber rings until the stiffness is removed, greater volume increases are obtained, *i. e.*, we obtain points on the true extension of these curves. In the

same way higher elongations could be obtained on the tensile testing machine.

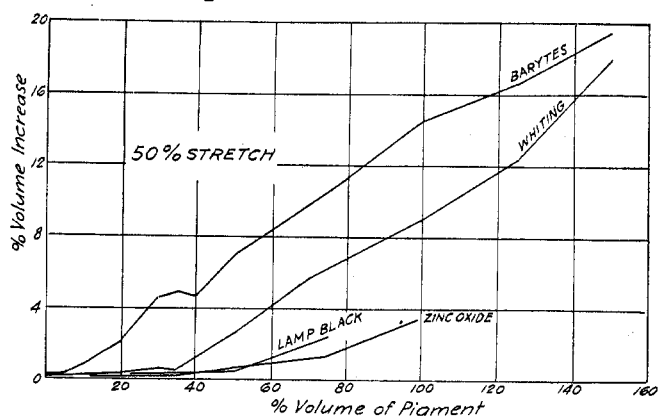


FIG. VIII

(II) WHITING—The curves for this series of compounds show that up to 40 volumes of whitening the percentage increase is comparatively small, then there is a sudden jump in volume increase with further addition of pigment, until at 150 volumes the whitening gives almost equal results to barytes. This probably is due to agglomeration of the pigment particles when present in large amounts. It should be noted that these curves are plotted on a more open scale of per cent-volume increase than that of the barytes.

(III) ZINC OXIDE—The trend of the zinc oxide curves up to 30 volumes is identical with that of the basic mix, although the ultimate elongation is reduced as much as 250 per cent. This shows that there is a strong adhesion of the rubber to the particles of zinc oxide, which imparts additional strength to the basic mix, but which reduces the ultimate elongation on account of the dilution of the rubber. This phenomenon classifies zinc oxide physically with the finer pigments, lampblack and carbon black. The upward shift of the curves for volumes above 30 indicates a rapid growth of agglomerated masses of particles which greatly reduces the tensile strength of these compounds. The shape of the almost complete 125-volume curve indicates that the large extrapolations of the other curves are approximately correct.

(IV) CHINA CLAY—The range of volumes experimented upon is not so large, but there is indicated an increase in volume for the low percentages of pigment. The open scale of "volume increase" to which these curves are plotted should be noted. The trend of these low volume curves away from the basic mix curves shows that the addition of china clay to rubber lowers the tensile strength in the compounds.

(V) RED OXIDE—The red oxide, being a finer pigment than china clay, shows less volume increase under strain. Also, departure from the curve of the basic mix shows a weakening effect upon the compound.

(VI) LAMPBLACK—The volume increase of the lampblack compounds is graduated proportionally to the content of lampblack up to 50 volumes. The 75-volume compound shows a considerable rise of volume increase, which indicates a rapidly increasing ag-

glomeration of the particles. This means that the limit of ability of the rubber to wet each particle of lampblack has been reached at 50 volumes, and above this volume the rubber surrounds groups of particles, instead of embedding each particle individually.

(VII) CARBON BLACK—A 30-volume content of carbon black lowers the ultimate elongation of the rubber to 530 per cent, while the same volume of lampblack lowers it to 420 per cent. This indicates a greater weakening effect of the lampblack on the rubber, although the volume increase under equal strain is less.

CURVES FOR 50 PER CENT AND 100 PER CENT STRETCH—Figs. VIII and IX show the property of volume increase in a different light. Here the variation of percentage volume increase is shown on a "volume of pigment" base for constant elongations of 50 per cent and 100 per cent. These curves are really a more distinct representation of the growth of agglomerated masses of pigment as the volume of pigment is increased. It will be noticed that at 100 per cent stretch the whitening and zinc oxide curves tend to approach the barytes curve, due to the more rapid formation of agglomerated masses of these pigments than of those of the barytes. Since the average particle of whitening has only one-eighth the volume of the average particle of barytes, it would require an agglomeration of the whole body of whitening into average groups of eight particles each to cause the whitening curve to meet the barytes curve, or multiples of eight, if there already existed an agglomeration of the barytes particles.

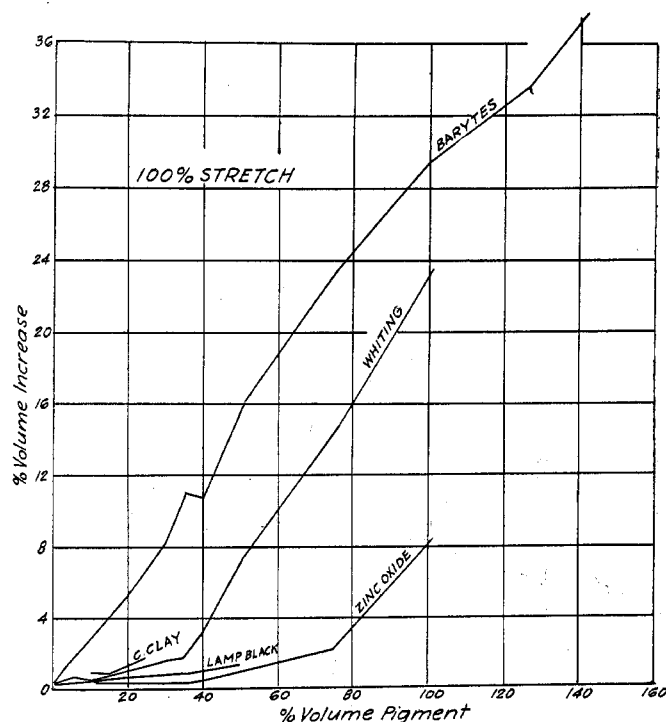


FIG. IX

This agglomeration of the pigment particles and the phenomena connected with it are of vital importance, since the sudden growth of agglomerated particles at certain volumes may be coincident with a rapid in-

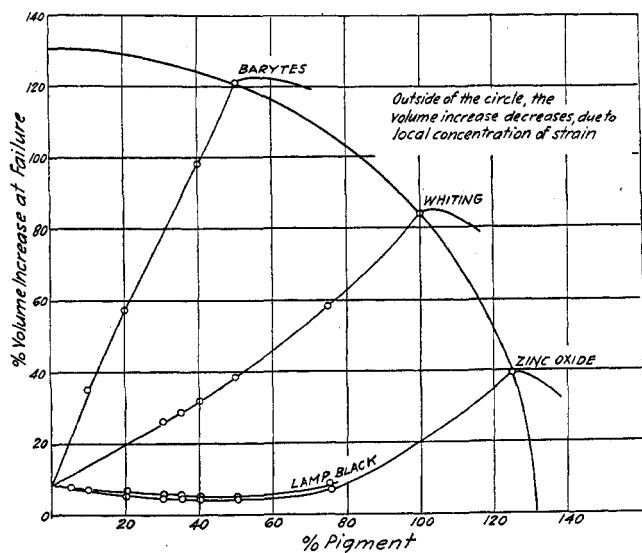


FIG. X

crease of hysteresis, due to the friction when the rubber body is distorted, among those particles which are in dry contact with each other. Conversely, any means of reducing the agglomeration of pigment should also be the means of reducing the hysteresis, such as the method of milling, and the use of solvents to reduce the viscosity of the rubber while mixing in the pigment.

Fig. X shows the percentage volume increase at failure on a base of percentage pigment, plotted up to the point of maximum volume increase, which takes place, as mentioned before, when local contraction of area occurs. These maximum points, as shown for the three pigments, barytes, whiting, and zinc oxide, lie approximately on a circle having the origin as center. The lampblack curve cannot be extended sufficiently far to reach the maximum volume increase due to the inability of the rubber to absorb large quantities of lampblack. The curves for china clay, red oxide, and carbon black are not shown, but as far as they have been obtained, they fall between whiting and zinc oxide, the china clay lying highest and the carbon black lowest of the three.

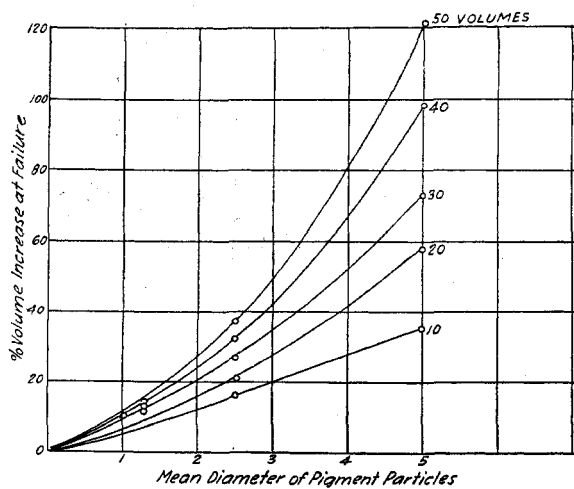


FIG. XI

Fig. XI undoubtedly shows the real explanation of the variability of the pigments from the volume increase standpoint. They show that, with the exception of zinc oxide, the greater the mean diameter of the pigment particles, the greater is the volume increase under strain. A confirmation of this statement was the result of a test on four samples of barytes compounds containing equal volumes of barytes of different degrees of fineness. The different grades were prepared by allutration in water. The compound containing the finest grade of barytes showed the least volume increase under strain. This was a critical test which eliminated every other variable but the size of the pigment.

### THE EXPANSION OF RUBBER COMPOUNDS DURING VULCANIZATION<sup>1</sup>

By C. W. Sanderson

FISK RUBBER COMPANY, CHICOPEE FALLS, MASS.

Received October 29, 1919

The extent to which rubber compounds will expand when subjected to the heat of vulcanization is of importance in the molding of rubber goods. As far as published results go, however, there are no available data on the value of the coefficient of expansion of rubbers of different compositions.

The work was undertaken by us primarily from a practical point of view, with the object of determining whether or not use could be made of an expansion test in distinguishing between stocks which move freely and mold well and those which do not mold well and are characterized as being "dead." Other possibilities suggested themselves and although the results are by no means complete or beyond question, they are set forth as we have found them.

#### APPARATUS

A special apparatus was designed for the investigation (Fig. 1). It consists of a hollow steel cylinder which may be filled with rubber and which is surrounded by a steam-jacket. The top surface of the rubber is the only surface free to move when the rubber is heated, and it acts against a piston and spring. The motion is transmitted through a magnifying lever to a recording pencil. The piston, spring and recording mechanism were taken from a Crosby steam indicator gauge and made over to fit the apparatus. Above the piston is a place for a spring to keep pressure enough on the rubber so that it will not "blow." Ten-, 50- and 100-pound springs were used. The 10-pound spring was hardly strong enough to prevent blowing. The use of the 50- and 100-pound springs will be mentioned later.

In making the determinations of the expansion the rubber was heated at a constant rate, usually 20° per 5 min. The recording cylinder was advanced at each interval and from the values on this graph smooth curves could be drawn.

The dimensions of the steel cylinder were:

Diameter, 0.7978 in.

Height, 2.0 in.

<sup>1</sup> Paper presented before the Rubber Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.