Some Physical Properties of Rubber Compounded with Light Magnesium Carbonate^{1,2}

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Light magnesium carbonate is a light inorganic filler for rubber which has heretofore received little attention from American rubber technologists. In this paper there are given data showing that this material behaves as a typical reinforcing pigment, increasing the tensile strength, hardness, stiffness, and resilient energy capacity of rubber in which it is compounded. Comparison has been made between the physical properties of rubber compounded with magnesium carbonate and with other commercial rubber reinforcing fillers, including zinc oxide, gas black, prepared china clay, and colloidal barium sulfate. The results indicate that magnesium carbonate is exceeded in reinforcing power only by gas black.

Special consideration is given to the principal disadvantage of magnesium carbonate in rubber, viz., the property of high permanent set imparted to the vulcanized product, which is attributable to the definite crystalline or nonamorphous character of the particles. The author believes that the application of the principles of colloid chemistry to the conditions of the commercial precipitation process will enable this material to be prepared in an amorphous form which will make it much more valuable as a rubber compounding material, by reducing the objectionable permanent set and enhancing the tensile strength and toughness of rubber compounded with it.

LIGHT magnesium carbonate, the chemically precipitated basic hydrated carbonate of magnesium, is not a new compounding material to the rubber industry of this country although it has never had the extensive and general use as a toughening and reinforcing filler in American rubber compounding practice which it has found in British and Continental rubber manufacturing. The English rubber chemist's knowledge of and experience with magnesium carbonate is, therefore, considerably greater than our own. The reason for this may be explained by the fact that rubber compounding practice has developed along rather different lines in this country from in Europe, particularly with respect to the adoption of gas black as a reinforcing pigment. The future for gas black does not seem particularly encouraging at this time owing to the rapidly decreasing supply of natural gas available for its manufacture and to various actual or threatened legislative restrictions on the use of natural gas for the production of this material. The rubber industry is, therefore, very properly concerned with the discovery of new, light, inorganic, "active" fillers, and is interested in the further development and improvement of those which it already uses. Some American rubber manufacturers use considerable amounts of magnesium carbonate; others use very little or none at all, and it is believed, therefore, that some of the data here presented, on the physical properties and mechanical behavior of rubber compounded with light magnesium carbonate, will be of interest to those rubber technologists who have not previously given this material much attention or study.

The raw material for the manufacture of light carbonate of magnesia is dolomite rock, high magnesian-limestone, of which

there are enormous deposits in this country and, in fact, all over the world, so that there is no possibility of a future exhaustion of the raw material supplies for the manufacture of this product. A number of the deposits which are being worked commercially at the present time are in Pennsylvania, convenient to the manufacturing centers and markets of the Eastern and Central States. The companies now manufacturing light magnesium carbonate have producing capacity ample to supply any possible needs of the rubber industry without the installation of additional equipment. It should be remarked that, since magnesium carbonate is manufactured by a chemical precipitation process, its production cost will necessarily be greater than the costs of naturally occurring materials which require only a minimum amount of treatment to prepare them for use in compounding; the principal factors in the cost of magnesium carbonate being coal and labor, both of which items may be subject to some downward revision in the future.

Basic magnesium carbonate may be manufactured from any soluble magnesium salt by treating it in solution with an alkali carbonate, but the product so obtained is likely to be rather variable in composition and not extremely finely divided. The light carbonate offered to the rubber industry as a compounding material is prepared commercially in this country by the rapid heating of a solution of magnesium acid carbonate, and this process gives a very white, soft, bulky, finely divided form of the material, of uniform composition. The formula ordinarily given for the composition of the substance in the dry form is $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, but numerous analyses of the commercial material seem to indicate that it corresponds actually more nearly to such a formula as: $11\text{MgCO}_3 \cdot 3\text{Mg}(\text{OH})_2 \cdot 11\text{H}_2\text{O}$. The composition varies slightly according to the conditions obtaining in the production processes, particularly the concentration of the magnesium acid carbonate solution and the rate of heating of this solution, but under rigid control of the process the composition of the product will be constant. The commercial carbonate of magnesia is usually practically chemically pure, containing only traces of iron and alumina, no silica, and considerably less than 1.0 per cent of lime as calcium carbonate. On samples free from hygroscopic moisture it gives an ignition loss varying from about 54.5 to 56.8 per cent. At ordinary temperatures it is inert to most chemical influences except the action of acids, which dissolve it, forming soluble magnesium salts. No decomposition takes place on heating to temperatures below 265°C . (509°F .), a temperature much above that to which rubber products may be safely subjected, either in the vulcanization process or subsequently. It seems probable that the water in the above chemical formula for the material is not ordinary water of crystallization, but water of constitution.

With regard to its use in rubber, its volume cost per unit of reinforcing effect, or per cubic foot of rubber compounded with it, will be small, owing to its low density, and considerably less than that of heavy pigments, such as zinc oxide or barium sulfate.

Light magnesium carbonate has an absolute density of about 2.18, although some figures rather lower than this have been given. It is, therefore, one of the lightest of the min-

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² The data presented in this paper summarize the more significant portions of the results of an investigation of this material, carried out at the Mellon Institute of Industrial Research, for the Magnesia Association of America.

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eral inorganic fillers and gives a vulcanized rubber of low specific gravity, although somewhat higher than that given by gas black or lampblack. The individual crystals have a distinct acicular crystal form and are very friable. Examination under the microscope shows an average particle size of somewhat less than a micron, with a few larger crystals, although the particle size varies somewhat in the product of different manufacturers and will depend on the control of the conditions of precipitation and upon the completeness of the pulverization process. The carbonate shows only a very slight solubility in water, about 0.035 g. of the oxide dissolving in a liter, and giving the solution a reaction alkaline to thymolphthalein indicator.

Except with respect to investigations of the effects of various mineral and organic accelerators, there has been, until recently, but scant information regarding compounding ingredients in the literature of rubber technology. Toughening and reinforcing fillers were, of course, always differentiated in the practical work of the rubber technologist from ordinary coarse fillers and inert pigments, but very little data comparing the actual physical behavior of different fillers in rubber were published until W. B. Wiegand⁴ studied the effects on the stress-strain relationships of rubber, obtained with several common compounding materials, and brought forward the concept of energy of resilience in rubber. Wiegand divides all rubber fillers into two groups, according to whether the average particle size is extremely small or whether the particles are relatively coarse. The reinforcing effect of rubber pigments he considers to be a function of the surface area exposed to the rubber by unit volume of the material, aside from specific surface and cohesion effects and, therefore, dependent upon the fineness of division of the particles. He succeeded in showing that all the rubber fillers he studied, which modify the stress-strain curve in such a way as to enable the rubber to exhibit high total resilient energy, are those which are very finely divided. These fillers, which are relatively few in number, he designates as "active" fillers or reinforcing pigments, whereas the coarse fillers, which do not greatly modify the stress-strain curve and, therefore, only dilute the rubber and attenuate its tensile strength, ultimate elongation, and resilient energy capacity, in whatever proportion they may be used, he refers to as physically inert fillers. Resilient energy capacity, according to Wiegand, is a measure of the reinforcing or toughening effect obtained with various fillers and he relates it also in a theoretical way to abrasive wear resistance.

Wiegand did not include light magnesium carbonate among the rubber pigments studied by him, and aside from mere occasional mention of its action as a mild accelerator of vulcanization, the work of C. O. North⁵ seems to be the only investigation so far published in which the behavior of this material in rubber is described. North made a comparative study of zinc oxide, gas black, magnesium carbonate, lithopone, barytes, and tripoli flour, in mixes containing rubber and sulfur only, with respect to the effects of these fillers on the physical properties of the vulcanized rubber. He found that, in the type of basic mix he used, magnesium carbonate gave its maximum effect on tensile strength at six volumes of the carbonate to each one hundred volumes of rubber, this tensile being higher than that obtained with any other filler, except gas black. For proportions of magnesium carbonate between six and fifteen volumes per one hundred of rubber, he obtained values for tensile strength "corrected" to the basis of 100 per cent rubber in the stock, which were equal to or slightly greater than the highest values obtained for zinc oxide, but not as great as given by larger proportions of gas

black. For the same proportions of magnesium carbonate he obtained calculated values for tensile product, and for tensile product "corrected" to 100 per cent rubber, which were greater than similar values obtained for gas black, zinc oxide, or the other fillers studied. This last result means, of course, that magnesium carbonate gives rubber having high tensile

FIG. 1

strength combined with high ultimate elongation values. North also gave data showing the high permanent set given by magnesium carbonate and attributed to this effect the fact that American compounders had not used this filler to a very great extent.

EXPERIMENTAL METHOD

All the rubber samples described in this paper were prepared under experimental conditions maintained as nearly uniform as possible, with respect to the composition of the basic mix, incorporation of the fillers on the mill, calendering, and vulcanization. The basic mix adopted had the following composition in parts by weight:

First quality pale crepe.....	100
Litharge.....	30
Sulfur.....	5

This basic mix is similar to that used by Wiegand in the investigation referred to above, except that pale crepe rubber was used in place of fine Para. The difficulty in obtaining a satisfactory grade of cleaned and dried Para at the time this work was begun made this change seem advisable. In parts by volume this mix contains:

First quality pale crepe.....	100
Litharge.....	3
Sulfur.....	2.5

The purpose of using this type of basic mix containing a considerable excess of litharge as accelerator was to make it possible to cure all the samples for a fixed period of time and to avoid the preparation of a series of cures for each proportion of filler of which the effect was to be studied. The values obtained for physical properties should also be somewhat nearer to those which can be produced in the factory than is likely to be the case in samples cured for a longer period with sulfur only, where the harmful effects of the longer period of heating on the samples may vitiate the results.

In this work two different lots of pale crepe rubber were used. The first lot, used in preparing samples compounded with various proportions of magnesium carbonate, gave a practically flat state of cure curve (judged from tensile strength values) over a curing period from 40 to 50 min. at 42 lbs. steam pressure (143° C.) when the samples were vulcanized in one-eighth inch thick sheet-molds in a press at 2500 to 3000 lbs. pressure. The basic mix sample showed its

⁴ *Can. Chem. J.*, **4** (1920), 160; *THIS JOURNAL*, **13** (1921), 118.

⁵ *India Rubber World*, **63** (1920), 98.

optimum aging qualities, both with respect to accelerated aging and weathering tests, when cured 45 min., and the same was found to be the case when the stock contained 15 volumes magnesium carbonate, and this was, therefore, selected as the curing period for all samples prepared from this lot of rubber. The second lot of rubber used in preparing stocks in which magnesium carbonate and other fillers were compared, was found to give its optimum cure, both with respect to tensile and aging qualities at a 49-min. period, which was, therefore, adopted as the best cure for all samples prepared from that lot. It was found, in curing samples prepared from both these lots with sulfur only, that both were decidedly slow curing in the absence of an accelerator. No difficulty was experienced in obtaining satisfactory cures in the litharge-pale crepe mix described above and the results obtained may easily be duplicated. The excess of litharge used was sufficiently great so that no difference in the cures when larger proportions of magnesium carbonate were used was observed, although North's⁵ data showed that in a rubber-sulfur mix the accelerating effect of the larger proportions of magnesium carbonate was quite appreciable. Rubber cured with an excess of litharge accelerator was found to be considerably stiffer and much less extensible than when cured with sulfur only.

Three series of rubber samples were prepared to obtain the data given in this paper. In the first series the samples were compounded with proportions of magnesium carbonate varying from three to forty volumes per one hundred volumes of rubber in the compound. In the second series light magnesium carbonate in the proportion by volume found to give the maximum reinforcing effect (nine volumes) was compared with four other inorganic reinforcing fillers in the same volume ratio: zinc oxide, gas black, prepared china clay, and colloidal barium sulfate. Rubber stocks compounded with mixtures of light magnesium carbonate with these same fillers, varying the proportions by regularly spaced increments, but maintaining the same total number of volumes of filler in each compound, were also studied. The third series included samples compounded with twenty volumes magnesium carbonate, with twenty volumes zinc oxide, and with various mixtures of these two fillers, having in each case a total of twenty volumes filler in the compound.

The materials used in the preparation of these rubber stocks were the best standard materials available in the market for use in rubber compounding, including zinc oxide of the highest quality, a superior grade of gas black, and impalpable sulfur. The china clay was a finely divided material especially prepared for rubber compounding and the colloidal barium sulfate was a high quality, highly dispersed product much superior to ordinary barytes. The magnesium carbonate was the ordinary light technical grade.

FIG. 2

PHYSICAL TESTS

The physical tests carried out upon all the samples discussed in this paper included:

TENSILE STRENGTH AND ULTIMATE ELONGATION—These values were obtained on a Scott testing machine using standard 0.25-in. width dumb-bell test strips. The results accepted as representing the actual values for these properties are in every case the average of the results from not less than five samples from the same sheet, the principle having been adopted of discarding results which were at great variance with the average and those in which premature failure of the test piece was obviously due to

FIG. 3

flaws in the sheet. Complete stress-strain curves for all the samples were obtained on the Scott testing machine, using two observers to secure the readings for the points on the curve.

TENSILE STRESS AT 300 PER CENT ELONGATION—The value for the load at 300 per cent elongation for each sample was obtained directly from the stress-strain curve plotted from the data obtained as just described.

TOTAL ENERGY OF RESILIENCE, AND ENERGY ABSORBED AT 300 PER CENT ELONGATION—Total energy of resilience was obtained according to the method of Wiegand, calculating from the area between the complete stress-strain curve and the elongation axis, and using a planimeter to determine this area. The energy absorbed by the rubber up to an elongation of 300 per cent was determined in the same way, using the planimeter to determine the area between the portion of the stress-strain curve below 300 per cent elongation, and the elongation axis.

PERMANENT SET—This property was determined by the method recommended by the Physical Testing Committee of the Rubber Division, using three stretches of the test piece to 60 per cent of the breaking length, with 5-min. rest intervals, and a final 10-min. rest before reading the permanent length deformation. The values given are the average of several tests on strips from the same sheet.

HARDNESS—The hardness of the samples was determined by means of a "durometer," a simple instrument depending on the penetration of a blunt point into the surface of the rubber sheet when a fixed pressure is applied. The range of hardness of vulcanized rubber is divided into an arbitrary scale, from "soft" at zero to "hard" at 100. The litharge-pale crepe basic mix used in this work gave a "durometer" hardness number varying from 40 to 42, depending upon the lot of rubber used. The hardness increases slowly with aging of the samples.

TENSILE PRODUCT—Calculated as tensile strength in lbs. per sq. in. multiplied by ultimate per cent length, and for convenience of numerical expression divided by 10,000.

ACCELERATED AGING TEST—All samples heated for 7 days at 71° C., in an oven through which a slow current of air was passing. This is considered to have approximately the same effect with respect to loss of tensile strength as 3.5 yrs.' aging under normal conditions.

WEATHERING TESTS—The samples subjected to this test were exposed to the atmosphere upon the roof of the building for 60 days during the summer months; this was a very severe test with respect to surface cracking tendencies and loss of tensile strength, and very few samples in the basic mix referred to above stood up well under this test.

TABLE I—DATA ON LIGHT MAGNESIUM CARBONATE

Volumes Light Mag- nesium Car- bonate to 100 Vol. Rubber	Compound Composition by Weight Per cent				Tensile Strength Lbs./Sq. In.	Tensile after Acceler- ated Aging Lbs./Sq. In.	Tensile after 60-Day Weathering Lbs./Sq. In.	Ultimate Elongation Per cent	Ult. Elong. after Acceler- ated Aging Per cent	Ult. Elong. after 60-Day Weathering Per cent	Perma- nent Set Per cent	Durometer Hardness Number
	Rubber	Sulfur	Litharge	Light Magnesium Carbonate								
0 ¹	74.0	3.70	22.3	0	2575	872	1600	696	490	585	5.5	40
3	70.4	3.52	21.2	4.9	2670	1190	1815	658	488	580	10.0	46
6	67.1	3.36	20.2	9.5	2740	1280	1950	655	425	545	20.0	50
9	64.1	3.20	19.2	13.6	3000	1430	1980	655	460	550	23.0	52
12	61.3	3.06	18.4	17.3	2910	1810	1960	610	495	530	24.0	55
15	58.7	2.94	17.6	20.7	2700	1560	1910	575	450	505	28.0	58
20	54.9	2.74	16.5	25.8	2650	1620	1290	560	438	375	30.0	62
25	51.5	2.58	15.5	30.4	2280	1660	1200	500	396	345	29.0	66
30	48.6	2.43	14.6	34.3	1910	1590	1280	460	304	305	27.0	69
40	43.7	2.18	13.1	41.1	1770	1390	1130	363	200	230	23.0	74

¹ Basic mix.

EFFECTS OF MAGNESIUM CARBONATE ALONE IN RUBBER

The data relating to the effect of magnesium carbonate on the physical properties of rubber are given in Tables I and II and represented graphically by the curves of Figs. 1 to 7, inclusive.

The behavior of magnesium carbonate, as shown in the stress-strain curves (Fig. 1), is seen to be that characteristic of a typical reinforcing pigment, as defined by Wiegand. With increasing volume additions of the pigment there is a very marked flattening of the curve, and when twenty volumes of the filler are present the curvature has practically disappeared and the stress-strain relationships are very nearly in accord with Hook's law for rigid materials, *i. e.*, proportionality of stress to deformation obtains. For certain proportions of the filler the tensile strength at rupture is increased above that of the basic mix, while at the same time the ultimate elongation is considerably decreased.

The tensile strength curve (Fig. 2) shows that this property of the rubber is increased up to a maximum at nine volumes of the filler per one hundred of rubber, and then falls off rather uniformly, becoming equal to that of the basic mix at about twenty volumes per one hundred of rubber (see Table I). Nine volumes of the carbonate correspond to about twenty-one parts by weight. With another lot of rubber, samples have been prepared containing twenty-five volumes of magnesium carbonate in which the tensile strength is equal to that of the basic mix. The curve for tensile strength after accelerated aging shows that this basic mix, containing an excess of litharge, does not stand up well under the heat test, whereas the heavily compounded samples, containing large proportions of magnesium carbonate and less rubber, age better than the lightly compounded ones. The curve for tensile strength after the 60-day weathering test is of a different character and practically parallels the curve for tensile properties before aging. Compounds containing between six and twelve volumes of magnesium carbonate show the highest tensiles after this aging test.

Ultimate elongation values for the stocks of the above series are represented in Fig. 3. The falling off on the elongation with increasing volume additions of magnesium carbonate is shown to be very nearly linear, up to forty volumes per one hundred of rubber (see Table I). After accelerated aging the decrease in elongation with increasing proportions of the filler is found to be uniform, though not linear, the elongation of every stock being considerably less than before aging, corresponding to the decrease in tensile which results from the application of this heat test. The 60-day weathering test gave quite different results. The lightly compounded samples retained after weathering the greater part of their original elongation, while the heavily compounded samples were much stiffer after this test than before. This difference in stiffness and hardness was observable to the eye, without carrying out tensile and elongation tests, and the heavily compounded samples also showed some surface checking and cracking, while those compounded with smaller proportions of magnesium carbonate did not.

Fig. 4 illustrates the effects of rubber compounding materials on the hardness of rubber, comparing light magnesium carbonate with gas black, zinc oxide, and ordinary ground magnesite, the last named being a coarse pulverized natural magnesium carbonate which is not a reinforcing pigment. Magnesium carbonate gives rubber hardness very much greater than that given by ground magnesite, somewhat greater than that given by zinc oxide, but considerably less than that given by gas black, which produces very hard and rigid compounds, even when used in rather small proportions (Table I). It appears, therefore, that there is a relationship between the hardness of rubber compounded with a particular filler and the reinforcing and toughening effect of that filler, which may perhaps be expressed in terms of the slope of the curve showing increase of hardness with successive volume increments of filler. This curve seems to be linear only for inert or coarse fillers, and not for reinforcing pigments.

The permanent set figures for rubber compounded with magnesium carbonate, in comparison with ground magnesite, zinc oxide, and gas black, are represented in Fig. 5. Magnesium carbonate shows a rapid increase in permanent set with successive volume increments, up to twenty volumes per one hundred of rubber, and then a uniform decrease from the maximum value (Table I). This decrease is explained by the fact that the ultimate elongation values for the heavily compounded stocks are small and, therefore, a 60 per cent extension of these samples is a much smaller actual stretch than in the cases of the more lightly compounded samples having higher elongation, and gives, therefore, a smaller result for the permanent set figure. Magnesium carbonate gives much greater set effects than either zinc oxide or gas black and greater still than ground magnesite. The latter gave no set figure higher than 12.0 per cent even up to fifty volumes of this filler. This, it appears, is due to the fact that even with smaller proportions of the material the set effect is not very great, and with larger proportions the great decrease in the final elongation corresponding to the diluent effect of this inert filler, permits low permanent set values to be obtained by this method of making the test.

High permanent set is an effect which seems to characterize in a degree all definitely crystalline substances which are used in compounding rubber, and the fact that magnesium carbonate particles have a definite crystal structure and acicular form is usually offered as the explanation of why magnesium carbonate gives high permanent set where other substances having approximately the same particle size do not show this effect. Zinc oxide, for example, although it possesses some of the properties of crystals, is amorphous in form and does not produce high permanent set. Let us consider the behavior of an individual crystal particle in rubber under stress, with particular regard to the internal structure of the vulcanizate. It may be assumed to start with that in freshly vulcanized rubber compounded with a substance such as magnesium carbonate, made up of small, definitely crystalline particles uniformly dispersed in the rubber, each particle is

in complete and uniform contact with the rubber matrix, *i. e.*, the rubber adheres closely to each crystal face. The particles will lie with their axes at various angles to the di-

Wiegand⁸ directed attention to the fact that when a stock containing one of the "active" fillers is stressed to rupture, a part of the energy required goes toward distorting the rub-

FIG. 4

rection of applied stress in the sample and when this stress is increased until the elongation is sufficiently great, say 60 per cent, as in the permanent set test discussed above, there will be a tendency for the particles to align themselves with their long axes in the direction of the applied stress. Very powerful shearing forces will then come into operation, acting between the plane surfaces of the crystal lying parallel to the direction of stress, and the rubber matrix to which each crystal face is united by cohesion forces. These surface forces vary with the physical and chemical nature of the crystalline substance to which the rubber is bonded, and probably also with the presence of other substances dispersed or dissolved in the rubber. When the bonding between the particles and the rubber has been broken and the filler particles have reoriented themselves in the mass, the rubber can never completely return to its original conformation and the individual particles will never reunite themselves to the rubber in the same degree as they were when the rubber was first vulcanized.

Visible evidence of the separation of the magnesia particles from the rubber matrix may be obtained by stressing a sample cured with sulfur only. The sample will be practically translucent until blooming takes place, and when stretched there is a pronounced and permanent whitening, the result of the change in the refraction of the light passing through the rubber after the particles have become readjusted in the mass.

The behavior of an amorphous substance in rubber will be distinctly different, because the particles are irregular in surface contour and offer no plane surfaces to the rubber, which will, therefore, attach itself to the particle at many points of this irregular surface. The surface forces, therefore, instead of being exerted at plane surfaces and in one direction only, perpendicular to that surface, will be exerted in many directions, owing to the approximately spherical or irregular shape of the amorphous particle. Schippel⁶ showed that compounded rubber when stressed gave an increase in volume, which he explained as being due to the formation of vacua at the poles of the particle in the direction of the applied stress. This was confirmed by Green,⁷ who was able to show by examination of microsections of compounded rubber the actual formation of such vacua in rubber under strain, but his experiments indicated that no vacua were formed with fine pigments in rubber when compounded in small percentages.

FIG. 5

ber phase itself and a considerable part toward tearing apart the rubber matrix and the imbedded pigment particles. In the case of an amorphous particle in rubber under stress there is only a slight separation of the rubber to form vacua at the poles and since no plane surfaces are subjected to shearing stresses, there is not such a pronounced tendency for the rubber matrix to break its bonding to the individual particles, entirely aside from specific cohesion forces exerted between the rubber and the particle surface. Consequently there will not be a great tendency for the particles to change their orientation in the mass and give a volume increase and high permanent set. The conclusion seems unavoidable, therefore, that an amorphous light magnesium carbonate would give less permanent set than is obtained with the crystalline material manufactured by the present process, and the modification of the precipitation process to produce a material of less pronounced crystalline characteristics and, if possible, even smaller particle size is being made the object of considerable study at the Mellon Institute of Industrial Research. If this can be accomplished it should make light magnesium carbonate of much greater value to the rubber compounding, and the writer hopes to have the privilege of presenting some results of the work along this line at the next meeting of the Rubber Division.

Data representing the reinforcing effect of magnesium carbonate are shown in the tensile product and total resilient energy curves of Fig. 6. The tensile product values are not as high as those obtained by North, owing to the higher extensi-

FIG. 6

⁶ THIS JOURNAL, 12 (1920), 33.

⁷ India Rubber World, 65, (1922), 350.

bility of the rubber-sulfur mix used in his work, as compared with that of this litharge-pale crepe mix. The curve has, however, approximately the same form. Tensile product

FIG. 7

reaches a maximum at nine volumes and becomes less than that of the basic mix at fifteen volumes; it is never very much greater than that of the basic mix. Quite different results are obtained with regard to resilient energy. (See Table II.)

TABLE II—DATA ON REINFORCING EFFECT OF LIGHT MAGNESIUM CARBONATE

Volumes Magnesium Carbonate to 100 Vol. Rubber	Tensile Product	Total Resilient Energy Ft. Lbs./Cu. In.	Resilient Energy Per cent of Base Mix	Tensile Stress at 300 Per cent Elong. Lbs./Sq. In.	Energy Absorbed at 300 Per cent Elong. Ft. Lbs./Cu. In.
0	205	318	100	150	11.7
3	205	355	112	225	16.7
6	208	425	134	355	20.5
9	227	475	149	455	31.7
12	212	438	138	505	35.0
15	197	398	124	600	39.0
20	174	407	128	770	50.0
25	137	355	112	910	63.4
30	107	265	83	1050	71.3
40	82	233	73	1405	104.0

The maximum is reached at nine volumes, the same maximum as for tensile strength and tensile product, and the total resilient energy is then 49 per cent greater than that of the basic mix. Resilient energy capacity of the compounds does not become less than that of the basic mix until more than twenty-five volumes of magnesium carbonate are incorporated.

For comparison purposes, the tensile product and total resilient energy curves for rubber compounded with various proportions of ground magnesite have also been plotted. The two curves are found to be almost identical in form, and the plotted values for tensile product and resilient energy decrease uniformly with each successive addition of this inert

FIG. 8

filler, being in every case less than the values for the basic mix. This illustrates the difference in mechanical qualities between rubber compounded with reinforcing pigments and with inert fillers. From a study of these curves the conclusion seems logical that for inert fillers either tensile product or resilient energy is a satisfactory index of the quality of the vulcanizate, but that for rubber compounded with "active" fillers resilient energy capacity gives a more accurate means of evaluation than does the tensile product, because tensile product measures only the actual stress at break, correcting for the decrease in the cross section of the test piece under stress, whereas resilient energy capacity takes into account the change in the character of the stress-strain curve, and it is this indication of the stress-strain relationships which determines the alteration in the physical properties of the product.

W. W. Vogt⁹ has directed our attention to the fact that if the tensile stress at 300 per cent elongation is plotted against

FIG. 9

the number of volumes of filler per one hundred volumes of rubber, the curve obtained is linear, showing an increase in load with increasing amounts of filler. The slope of this line, he concludes, is a measure of the stiffening or reinforcing action of the filler. On Fig. 7 will be found curves showing the relation between tensile stress at 300 per cent elongation for magnesium carbonate and for ground magnesite. The magnesium carbonate curve has a much greater slope than the ground magnesite curve, which is to be expected, corresponding to its greater reinforcing action. The slope of this line indicates the rate of flattening of the fore part of the stress-strain curve with increasing volume additions of the filler which is being studied. The magnesium carbonate curve is linear throughout and the ground magnesite curve is linear up to thirty volumes, and then flattens out somewhat.

On the same graph, for comparison purposes, there have been plotted the values for the resilient energy absorbed at 300 per cent elongation by rubber compounded with various proportions of light magnesium carbonate, and also with ground magnesite. The curves for absorbed energy at 300 per cent elongation are very similar in form to those just discussed above for tensile stress at 300 per cent elongation, although they are not perfectly linear. The spread between the absorbed energy curves for magnesium carbonate and ground magnesite is almost identical with that between the curves for tensile stress at 300 per cent elongation for the same fillers, and since the energy capacity of the rubber at 300 per cent elongation also depends upon the flattening of the fore part of the curve, the slope of the line

⁹ India Rubber World, 65 (1922), 347.

TABLE III—DATA ON MIXTURES OF LIGHT MAGNESIUM CARBONATE WITH OTHER REINFORCING PIGMENTS

VOLUMES FILLER TO 100 VOLUMES RUBBER				Colloidal Barium Sulfate	Tensile Strength Lbs./Sq. In.	Tensile after Accelerated Aging Lbs./Sq. In.	Ultimate Elongation Per cent	Ult. Elong. after Accelerated Aging Per cent	Permanent Set Per cent	Durometer Hardness Number
Magnesium Carbonate	Gas Black	Zinc Oxide	China Clay							
0 ¹	0	0	0	0	2650	1200	738	550	6.0	42
9	0	0	0	0	3400	2275	650	550	19.5	51
6	3	0	0	0	3440	2070	638	505	17.0	52
3	6	0	0	0	3600	1710	635	380	16.5	54
0	9	0	0	0	3450	1190	600	345	9.5	53
6	0	3	0	0	3290	2290	665	610	15.0	50
3	0	6	0	0	3285	2410	675	370	12.0	50
0	0	9	0	0	3000	1760	665	600	10.5	49
6	0	0	3	0	3300	2060	653	550	18.5	50
3	0	0	6	0	3200	2080	615	325	17.5	50
0	0	0	9	0	3000	1780	600	485	16.0	49
6	0	0	0	3	3075	2040	677	580	13.5	50
3	0	0	0	6	3020	1760	653	540	12.0	49
0	0	0	0	9	2810	1650	700	500	9.0	44

¹ Basic mix.

showing the change in this quantity with successive increments of filler also measures the rate of flattening of the lower portion of the curve and may properly be considered an index of the reinforcing action of the pigment whose effect is being investigated. This would enable the investigator to make a direct comparison between the reinforcing effects of different pigments on the basis of energy relationships rather than on tensile stress alone.

COMPARISON OF MAGNESIUM CARBONATE WITH OTHER REINFORCING PIGMENTS

Light magnesium carbonate gives its maximum reinforcing effect with respect to tensile strength, tensile product, and resilient energy capacity at nine volumes per one hundred of rubber. Magnesium carbonate was therefore compared at this volume ratio with equal proportions by volume of zinc oxide, gas black, prepared china clay, and colloidal barium sulfate. The effects of mixtures of magnesium carbonate with each of these fillers upon the physical properties were also studied, having a total of nine volumes filler in each compound, and varying by three-volume increments the proportions of magnesium carbonate and the other reinforcing pigments. These data, as given in Tables III and IV, and Figs. 8 to 18, inclusive, show in graphic form the changes in physical properties. It must be understood, of course, that nine volumes of the pigments other than magnesium carbonate do not represent the point of maximum reinforcement, which in the case of gas black, for example, is not reached until about twenty volumes are incorporated.

In Fig. 8 are represented the stress-strain curves for mixtures of magnesium carbonate and zinc oxide. Magnesium carbonate is shown to give a greater stiffening effect than zinc oxide in this volume ratio. The stress-strain curves of Fig. 9 for mixtures of magnesium carbonate and china clay

show that magnesium carbonate has a stiffening action which is very slightly less than that of china clay. Fig. 10 gives stress-strain curves for similar mixtures of magnesium carbonate with colloidal barium sulfate, which show that magnesium carbonate has a much greater reinforcing and stiffening action than colloidal barium sulfate. Stress-strain curves for mixtures of magnesium carbonate and gas black are represented in Fig. 11. These show that gas black gives a stiffer rubber than magnesium carbonate, and that it has also a greater reinforcing action than china clay. In every case the mixtures of magnesium carbonate with the other reinforcing pigments give reinforcing effects intermediate between those obtained with either material in the same volume ratio alone, as shown by the relative positions of their stress-strain curves.

Tensile strength data for the compounds just discussed, represented by the curves of Fig. 12, show that magnesium carbonate compounded in the nine-volume ratio produces tensile strength somewhat greater than that given by zinc oxide or china clay in equal proportions, and considerably greater than that given by colloidal barium sulfate. The tensile with nine volumes magnesium carbonate is slightly less than that produced by nine volumes of gas black. The curve shows, and this has been confirmed by the preparation of several samples, that a mixture of six volumes gas black and three volumes magnesium carbonate per one hundred volumes of rubber gives a tensile value of 3600 lbs. per sq. in., considerably higher than can be obtained by the use of the same total volume of either filler alone in this basic mix. With the other reinforcing pigments, zinc oxide, china clay, and colloidal barium sulfate, there is a uniform falling off in tensile strength, with successive replacements of magnesium carbonate in the compound, by any one of these fillers (see data in Table III).

FIG. 10

FIG. 11

Fig. 13 shows the loss in tensile strength of these compounds resulting from the accelerated aging test (data given in Table

is quite definitely harder than the magnesium carbonate compound.

FIG. 12

III). Inspection of the curves makes it evident that in this basic mix stocks containing gas black do not stand up well under this heat test. The best aging samples are those compounded with mixtures of zinc oxide and magnesium carbonate, although the stock containing zinc oxide alone loses a greater proportion of its original tensile strength. Samples compounded with colloidal barium sulfate, with china clay, with gas black, and with mixtures of magnesium carbonate with these other materials show poorer tensile values after accelerated aging than was the case with the compound containing only magnesium carbonate. In so far as this test may be considered of value in determining the aging qualities of compounded rubber, it is evident that magnesium carbonate compares very favorably with these other reinforcing pigments. The magnesium carbonate sample has lost 33 per cent of its original tensile strength, while the other compounding materials show losses of from 41 to 65 per cent.

The hardness of rubber compounded with mixtures of magnesium carbonate and these reinforcing pigments is shown by the curves in Fig. 14 (see data in Table III). In this volume ratio magnesium carbonate gives a vulcanizate slightly harder than is produced by the same proportion of either zinc oxide or china clay, and considerably harder than that given by the same volume of colloidal barium sulfate.

This same volume of gas black gives a compound which

FIG. 14

FIG. 13

Fig. 15 shows just the sort of results with respect to permanent set with mixtures of magnesium carbonate and other reinforcing pigments which would be anticipated from the preceding data and discussion of the permanent set effect given by magnesium carbonate, since these other fillers are all more amorphous than the carbonate. The set with mixtures of china clay and magnesium carbonate increases almost linearly with increasing proportions of magnesium carbonate, although clay itself produces rather high permanent set. In the case of mixtures of gas black and magnesium carbonate the set increases more rapidly than in a linear ratio. The permanent set of the compound previously referred to, containing six volumes gas black and three of magnesium carbonate, is 17.5 per cent. It should be remarked that the compound containing nine volumes of carbonate, although it has a greater tensile strength than was given by the same volume of this filler in the other lot of pale crepe used in the preliminary study of its effect, gives a lower permanent set, only 19.5 per cent, as compared with 23.0 per cent.

The rate of increase in permanent set in the compounds containing mixtures of magnesium carbonate with zinc oxide and with colloidal barium sulfate is seen to be less than that corresponding to a linear ratio.

The resilient energy capacity curves, Fig. 16, show some interesting results. Magnesium carbonate shows higher resilient energy in this volume ratio than zinc oxide, china clay,

FIG. 15

TABLE IV—DATA ON REINFORCING EFFECTS OF MIXTURES OF MAGNESIUM CARBONATE AND OTHER REINFORCING FILLERS

VOLUMES FILLER TO 100 VOLUMES RUBBER					Tensile Product	Total Resilient Energy Capacity Ft. Lbs./Cu. In.	Resilient Energy Per cent of Basic Mix Energy	Tensile Stress at 300 Per cent Elongation Lbs./Sq. In.	Energy Absorbed at 300 Per cent Elong. Ft. Lbs./Cu. In.
Light Magnesium Carbonate	Gas Black	Zinc Oxide	China Clay	Colloidal Barium Sulfate					
0 ¹	0	0	0	0	222	398	100	200	25
9	0	0	0	0	255	573	144	600	68
6	3	0	0	0	233	580	146	650	70
3	6	0	0	0	265	637	160	715	77
0	9	0	0	0	242	568	142	775	80
6	0	3	0	0	252	570	143	565	62
3	0	6	0	0	255	567	142	525	57
0	0	9	0	0	230	513	129	490	52
6	0	0	3	0	248	593	149	650	73
3	0	0	6	0	228	540	136	700	71
0	0	0	9	0	210	500	126	745	79
6	0	0	0	3	239	524	132	515	57
3	0	0	0	6	228	490	123	485	50
0	0	0	0	9	225	467	117	380	44

¹ Basic mix.

TABLE V—DATA ON MIXTURES OF LIGHT MAGNESIUM CARBONATE WITH ZINC OXIDE

VOLUMES FILLER TO 100 VOLUMES RUBBER			Tensile Strength Lbs./Sq. In.	Tensile after Accelerated Aging Lbs./Sq. In.	Tensile after 60-Day Weathering Lbs./Sq. In.	Ultimate Elongation Per cent	Ult. Elong. after Accelerated Aging Per cent	Ult. Elong. after 60-Day Weathering Per cent	Permanent Set Per cent	Durometer Hardness Number
Light Magnesium Carbonate	Zinc Oxide	Gas Black								
0 ¹	0	0	2650	1200	1780	738	562	530	6.0	42
20	0	0	2890	1720	1290	560	460	413	23.0	64
15	5	0	2950	1720	1270	580	415	425	24.0	60
11	9	0	2830	1860	1540	585	463	494	15.0	58
7	13	0	2780	1780	1730	600	448	522	14.0	57
3	17	0	2840	1890	1970	595	500	535	16.0	56
0	20	0	2820	1760	1870	615	520	545	12.0	55
0	0	20	3950	1590	..	490	230	..	16.5	70

¹ Basic mix.

or colloidal barium sulfate, and equal to that of gas black. The high resilient energy values obtained with this proportion of magnesium carbonate are explained by the fact that this material gives high tensile strength, high elongation, and a pronounced flattening of the stress-strain curve;

therefore the area between the curve and the elongation axis is large and the calculated resilient energy is correspondingly great. The compound previously noted, containing six volumes gas black and three of magnesium carbonate, which gives high tensile strength, is also found to give the highest resilient energy value, 637 ft. lbs., or 60 per cent increase above the energy of the basic mix (see data in Table IV).

A comparison of the stiffening effect produced by magnesium carbonate and the other reinforcing pigments studied, on the basis of tensile stress at 300 per cent elongation, is given in Fig. 17 (based on data in Table IV). The curves representing tensile stress at 300 per cent elongation are all linear, for these mixtures of reinforcing pigments, and with respect to stiffening effect at this volume ratio of each filler, would place them in the following order of increasing reinforcing power: colloidal barium sulfate, zinc oxide, magnesium carbonate, china clay, gas black.

Fig. 18 gives curves for energy absorbed at 300 per cent elongation, making possible a direct comparison of these mixtures of magnesium carbonate with other reinforcing pigments, on the basis of energy values rather than on tensiles alone. The curves, it will be seen, lie in about the same relative positions and have approximately the same spread,

FIG. 18

FIG. 17

FIG. 18

FIG. 19

FIG. 20

FIG. 21

FIG. 22

but are not exactly linear. The order of increasing reinforcing power in the rubber is the same as given above for tensile stress at 300 per cent elongation, except that gas black and china clay are more nearly equal. (See Table IV.) It should be remarked, however, that this comparison takes into account only the stiffening effect on the fore part of the stress-strain curve and does not express the fact that higher tensile strength and total energy values are given by gas black and magnesium carbonate than can be obtained with clay. Schidrowitz and Burnand¹⁰ have pointed out, also, that great rigidity is not always associated with toughness (especially in the case of overcured samples) although this might be thought to be the case simply from a study of the stress-strain curves. Total resilient energy, however, takes into account both tensile strength and ultimate elongation in evaluating the physical properties, because for compounds, the lower portions of whose stress-strain curves are identical, the one which has the greatest tensile and elongation values will also give the greatest calculated resilient energy.

¹⁰ J. Soc. Chem. Ind., 40 (1922), 268t.

REINFORCING EFFECTS OF ZINC OXIDE AND MAGNESIUM CARBONATE AT TWENTY VOLUMES

The comparative study of magnesium carbonate and zinc oxide in more heavily compounded stocks, containing a total of twenty volumes filler, the data for which are given in Tables V and VI, and represented by the curves in Figs. 19 to 22, inclusive, confirms completely the results just discussed with regard to the reinforcing effect of magnesium carbonate in the nine-volume ratio.

The stress-strain curves, Fig. 19 (see Table V for data), show considerably greater stiffness for magnesium carbonate and for the compounds containing mixtures of zinc oxide with magnesium carbonate than for zinc oxide alone. There is a uniform decrease in ultimate elongation with increasing proportions of magnesium carbonate. For comparison purposes the stress-strain curve for twenty volumes gas black has also been plotted and is found to represent a much more rigid compound and one of higher tensile strength and lower ultimate elongation than is obtained by using equal volumes of either zinc oxide or magnesium carbonate.

VOLUMES FILLER TO 100 VOLUMES RUBBER			Tensile Product	Total Resilient Energy Capacity Ft. Lbs./Cu. In.	Resilient Energy Per cent of Basic Mix Energy	Tensile Stress at 300 Per cent Elongation Lbs./Sq. In.	Energy Absorbed at 300 Per cent Elong. Ft. Lbs./Cu. In.
Light Magnesium Carbonate	Zinc Oxide	Gas Black					
0 ¹	0	0	222	398	100	200	25.0
20	0	0	191	564	142	1230	128
15	5	0	200	573	144	1150	113
11	9	0	194	540	136	1040	100
7	13	0	195	547	137	980	95
3	17	0	197	522	131	860	88
0	20	0	202	531	133	810	77
0	0	20	194	574	144	1520	155

¹ Basic mix.