If samples are taken during the preliminary heating of the mixture referred to above, it may be observed when the major portion of the further refinable oil has separated. That condition obtains usually within the first hour or hour and a half, that is to say, at the end of the first stage when actual carbonization is near the minimum. Three layers form. The oil separates on top as indicated, and the excess concentrated acid accumulates at the bottom. The top layer is drawn off. The middle portion, which has not been heated high enough and long enough in contact with the concentrated acid to become carbonized and have its asphaltic nature destroyed, is a pasty mass, quite liquid at the temperature attained, and contains from 15 to 25 per cent (or even more) sulfuric acid. It is drawn off and is given one washing (1 : 5) with water. The diluted acid liquor is drawn off and sent to the concentrator. The asphaltic mass, in weighed portions, is run at once into a suitable mill, where it is mixed with the proper proportion (as determined by rapid analysis), usually in slight excess, of lime which has been freshly slaked with sufficient water to cause it to crumble into a powder. The mixture is then kneaded in the mill. Much heat is generated by the union of the free acid and calcium hydroxide, but not enough to char the material. If sufficient heat has not been generated during the mixing to render the mass fluid (due to low acid content), it may be heated to about 220° C., when as a fluid it may be run into a suitable receptacle for marketing. Finely divided limestone may be substituted for the slaked lime powder.

The asphaltic or bitumenic material present in the residuum has not been destroyed but simply incorporated with some 10 to 40 per cent of calcium sulfate, depending upon the amount of free acid present in the washed acid sludge.¹ The asphaltic or bitumenic material present may be readily extracted by the solvents generally used for dissolving those substances.

The whole mass exhibits the properties associated with asphalt, modified, of course, by the calcium salt produced. It becomes fluid when sufficiently heated and may be applied to metal, masonry, wood, etc. It adheres well and, from 6 months' test, is impervious to water. It mixes with rosin and other substances added to asphalt for particular purposes.

CONCLUSION

A by-product, formerly a nuisance, costing money to get rid of it, has been converted into a useful material possessing a commercial value.

REACTIONS OF ACCELERATORS DURING VULCANIZATION²

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The highest powered organic accelerators known to-day are the carbon bisulfide reaction products of

¹ The process is covered by U. S. Patent 1,234,985, July 1917.

² Presented before the Rubber Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

strong organic bases. Perhaps the best example is the piperidine salt of piperidyl-dithiocarbamic acid. The formation of this compound is shown by the following equations:

Due to the strong basic nature of piperidine, this salt is stable and may be isolated as such. Strong aliphatic bases such as dimethylamine also give stable dithiocarbamates which are very powerful accelerators.

Thiocarbanilide, which is perhaps the most widely used commercial accelerator, is formed by the same mechanism of reaction, there first being formed the aniline salt of phenyl-dithiocarbamic acid,

This aniline salt is extremely unstable due to the weak basic properties of aniline and cannot be isolated as such. The ammonium salt of this phenyldithiocarbamic acid may be isolated but decomposes on standing. The metallic salts of dithiocarbamic acids are much more stable according to Krulla.¹ The aniline salt, by loss of hydrogen sulfide, produces thiocarbaniide.

The stable dithiocarbamates above mentioned lose hydrogen sulfide in a similar manner when heated to the temperatures used in the vulcanization of rubber and produce thiourea derivatives. It is, therefore, quite possible that they may function as curing agents in the same manner as thiocarbonylthiourea.

André Dubosc² has stated that thiourea derivatives can "furnish in a colloidal state all the sulfur necessary for vulcanization." In checking up this statement it appeared at first that Dubosc was correct, but the cures obtained were soon shown to be due to free sulfur present as an impurity in the accelera-

¹ *Ber.*, **46**, 2669.

² *India Rubber World*, February 1, 1919.

tor used. Pure thiocarbanilide and pure dithiocarbamates do not vulcanize rubber in the absence of free sulfur either in a pure gum or high zinc oxide stock. We, therefore, are unable to agree with this investigator that the sulfur of such compounds is available for vulcanization.

There are some dithiocarbamates which liberate the free base by a heat decomposition, such, for example, as the liberation of dimethylamine by heating its carbon bisulfide reaction product. Since these free bases are evidently good curing agents, it is possible that they may function as accelerators after being liberated by a heat decomposition of the dithiocarbamates. It is, however, not the object of this paper to discuss the mechanism of the action of thiourea derivatives as accelerators. What we wish to show is that there are many accelerators not ordinarily classed with thiocarbanilide but which undoubtedly produce thiourea derivatives by reaction with sulfur during the vulcanization process, so that they may be classed as being similar to thiocarbanilide in their ultimate action.

In June 1913, J. Bastide was granted a patent¹ wherein he claimed methylene and ethylene compounds of aliphatic and aromatic amines as vulcanization accelerators. As specific examples he mentions methylene-diphenyl-diamine and phenyl-iminomethane, the latter being otherwise known as anhydro-formaldehyde-aniline or methylene-aniline. These two accelerators easily react with sulfur to form thiourea derivatives.

Methylene-aniline easily polymerizes to the di-, tri-, and probably higher polymers. We have found it convenient to consider it as the dipolymer and to take 210 as the molecular weight. It has been found that 210 g. of methylene-aniline will react with four atomic weights of sulfur, whereby one molecular weight of carbon bisulfide and one molecular weight of hydrogen sulfide are lost and that about 95 per cent of the product is thiocarbanilide. The reaction is represented by the following equations:

or

This reaction starts at about 130° C. and proceeds best at 150° C. The amount of carbon bisulfide liberated may be determined by condensing as much as possible and weighing. Any uncondensed carbon bisulfide vapors may be caught in aniline wash bottles which have previously been saturated with hydrogen sulfide. The amount of hydrogen sulfide may be determined by absorption in caustic. A small amount of aniline and other products are formed by side reactions. It is surprising how closely the weights of the products check up with the above equation.

¹ French Patent 470,883.

It is quite probable from the above data that methylene-aniline, when compounded as such, will generate carbon bisulfide during the cure. In the presence of basic amido compounds this carbon bisulfide should at once generate dithiocarbamates similar to those which have been shown by Ostromuiskii to have such high curing power. The curing power of methylene-aniline may, therefore, be due in part to the formation of dithiocarbamates formed from carbon bisulfide liberated slowly in the cure and a subsequent reaction with amido compounds which may be present, but its chief curing power is evidently due to the direct formation of thiocarbanilide. It must not be assumed, however, that methylene-aniline should therefore have as strong a curing power as thiocarbanilide. That this is not the case is undoubtedly due to the lag of the sulfur reaction during the cure.

Methylene-diphenyl-diamine produces several reaction products when heated with sulfur, the reaction proceeding easily at 140°-150° C.

(a) A certain amount of thiocarbanilide is formed, as illustrated by the following equation:

This reaction is desirable, but the yield is comparatively low.

(b) Methylene-diphenyl-diamine by heat alone loses aniline, probably by a semidine reaction with itself.

This reaction may be continued until the condensation has proceeded so far that one mole of the original compound has lost one mole of aniline. By reaction with sulfur before compounding and removal of such free aniline as may be formed, there is produced an accelerator of much greater curing power than the original material and which shows curing properties very similar to those of thiocarbanilide. One of the constituents of this reaction product is apparently the sulfur reaction product of Form IV.

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-thiobenzanilide.

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. Dubosc¹ 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 STRAIN¹

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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.

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

¹ Loc. cit.