negative values are obtained, owing to the liquors becoming more concentrated than they were originally, on account of the collagen abstracting water from them.

FIG. 2

We would state our belief, based upon our experience as presented in this and earlier papers, that the reaction between chromic sulfate solutions and hide substance is chemical and not physical, as contended by A. W. Davison.¹ If the adsorption were a simple physical process, *i. e.*, merely a partition of the chromic oxide and sulfuric acid between the solid hide substance phase and the solution phase, the curve should follow Freundlich's adaptation of Henry's law: $C_1 = kC_2^n$, which is parabolic in shape; whereas Miss Baldwin's and our experiments show that in a 2-day adsorption the curve begins to slope steeply downward after the concentration of the liquor exceeds approximately 16 g. of chromic oxide per liter in a solution of the composition of $\text{Cr}(\text{OH})\text{SO}_4$, and reaches a minimum when the concentration of chromic oxide is 147.5 g. per liter, this minimum being maintained at a concentration of 202 g. per liter. This minimum confirms the prediction of Wilson and Gallun in part. The most concentrated chrome liquor which we used was very thick and about as concentrated as is possible to handle; and therefore, we do not find it possible to test further their prediction that increasing concentrations beyond this minimum would cause greater fixation of chrome.

ACKNOWLEDGMENTS

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¹ J. Am. Leather Chem. Assoc., **12** (1917), 258

THE ACTION OF CERTAIN ORGANIC ACCELERATORS IN THE VULCANIZATION OF RUBBER—II¹

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One of the early patents² for the use of synthetic nitrogenous organic substances in the vulcanization of rubber refers to the dissociation constant of 1×10^{-8} as the dividing line between accelerating and non-accelerating bases. On the other hand, Peachey³ has pointed out that certain other substances which are not basic, or but slightly so, are also exceedingly active as accelerators. The number of examples in this class, however, is relatively small.

In the course of the experimental work described in this paper we have made a comparison of the sulfur coefficients of a type mixture vulcanized with the assistance of a number of accelerators closely related to aniline and for which the dissociation constants are known. We have also employed the hydrochlorides of two of these substances, relatively weak and strong bases, in order to observe the effect of the acid portion during the vulcanization. The results obtained and the conclusions drawn led us to employ the sulfides of ammonia as accelerators and vulcanizing agents.

Briefly summarizing these results, it was found that with the substances tested there was apparently no direct relationship between their dissociation constants and their excess sulfur coefficients or physical properties after vulcanization. In a closely related series, such as aniline and its methyl derivatives, the substance with the largest dissociation constant was found to be the most active. However, the relative activities of the members of this series were not proportional to their dissociation constants. Generally speaking, the activity of all of the substances could be traced to the amino group, and depended to a large extent upon whether or not substitution had taken place in this group. In this respect, they should probably be regarded as substituted ammonias, rather than as the more complex derivatives of other substances.

One effect of the basicity of two of the substances, methylaniline and *p*-toluidine, was determined with the hydrochlorides of these two substances. Our results showed that with substances of this type, the first effect of the base is to neutralize the retarding action of the acid formed in the decomposition of the salt during vulcanization. We had previously suggested this in a footnote in a former paper.⁴ We also found that when the acid liberated in the decomposition of such a salt is neutralized by other substances in the mixture, the activity of the hydrochloride is very close to that of the free base. These results are of particular interest, as Van Heurn⁵ has shown that, whereas ammonium carbonate is moderately active as an accelerator in a mixture of rubber and sulfur,

¹ Presented before the Rubber Division at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

² D. R. P. 280,198 (1914).

³ J. Soc. Chem. Ind., **36** (1917), 950.

⁴ Chem. & Met. Eng., **20** (1919), 420.

⁵ Comm. of the Netherlands Government for Advising the Rubber Trade and Industry, Part 6, 202.

ammonium chloride is inert. The former salt decomposes into ammonia and a weak acid, the latter into ammonia and a strong acid, according to the following reactions:

Our final experiments, wherein we found that in a closed system rubber is vulcanized by heating with ammonium polysulfide or ammonium hydrosulfide, were carried on in order to obtain a reaction mixture of undoubted basic character, which at the same time would include H_2S as one of the decomposition products. The function of H_2S in connection with the vulcanization of rubber has long been made a subject of controversy. In the present instance it may be regarded as a very weak acid.

Our results with ammonium polysulfide may be explained as due to the decomposition of this substance into ammonia, hydrogen sulfide, and sulfur, the latter substance being liberated in an active (nascent) form which readily combines with the rubber. The analogy between our results with ammonium polysulfide, and those obtained years ago by Gerard¹ with potassium tri- and pentasulfides, is taken up in greater detail in the experimental part of this paper. It is equally evident, however, that if this explanation is advanced in the case of ammonium polysulfide, vulcanization with ammonium hydrosulfide requires that this substance decompose not into ammonia and hydrogen sulfide only, but with the subsequent formation of a polysulfide which liberates sulfur in the active form.²

It has been shown by Bedford and Scott³ that many of the more complex substances which accelerate the vulcanization of rubber react with sulfur, with the liberation of H_2S and the formation of thiourea derivatives. In view of our results with the ammonium sulfides, the action of such thiourea derivatives would depend upon their ability to enter into a subsequent reaction with the H_2S formed, or the sulfur present in the mixture, with the formation of a polysulfide. Further, although the formation of a polysulfide in this manner would, to a certain extent, be dependent upon the basicity of the substance originally added as the accelerator, it is obvious that the dissociation constant of the reaction product would be a better indication of its activity than the dissociation constant of the original substance.

¹ R. Hoffer, "Treatise on Caoutchouc and Gutta-Percha" (trans. Brannet), H. C. Baird & Co., London, 1883.

² As an aqueous solution of NH_4HS was employed, the action of this substance may also be explained by its dissociation products. It would dissociate with NH_4^+ as the cation and HS^- the anion. As the HS^- ion itself is weakly acid, there would probably be many H^+ and HS^- ions and but few S^{2-} ions in the aqueous solution. The H^+ and S^{2-} ions in turn react to form H_2S . On the other hand, $(\text{NH}_4)_2\text{S}$ dissociates with NH_4^+ , the cation, and S^{2-} , the anion. The latter, in the presence of water, dissociates with the formation of OH^- and HS^- ions. Thus, NH_4HS dissociates with the formation of a greater number of H^+ ions than in the case of $(\text{NH}_4)_2\text{S}$, and consequently with a greater re-formation of H_2S . This may account for the difference in the relative activities of the two substances. The same may be true in the absence of water, as most organic accelerators are apparently soluble in rubber, the high dielectric constant of which indicates that this substance itself may be a good dissociating medium.

³ THIS JOURNAL, 12 (1920), 31.

In a previous paper¹ we have suggested that the activity of certain nitrogenous substances may be interpreted on the basis of a change in valency of the nitrogen, with the nitrogen functioning as a sulfur carrier. This suggestion was made to assist in correlating the nitrogen content with the activity of the substances employed, although, as pointed out in the above paper, results obtained by others already indicated that the sulfur is not necessarily attached to the nitrogen. While our present results show that vulcanization may be effected by polysulfide formation, they do not exclude the possibility of the active nitrogen group acting as a catalyst.

EXPERIMENTAL PART

The same general method of procedure was pursued in the course of this work as was previously reported in Part I.

The rubber was good quality, first latex, pale crepe, and the same lot was employed for all mixtures. All of the mixtures, the composition of which is shown at the head of the various tables, were mixed and vulcanized as before. Physical tests were made on a Scott testing machine of the vertical type. Sulfur estimations were made by our method, previously described in detail.²

The accelerators were purified, and melted or boiled at the temperature shown in the tables. All of the accelerators were compared on a molecularly equivalent basis, 0.01 g. molecule of the accelerator being added for each 100 g. of rubber in the mixture.

EXPT. I.—This experiment was carried on in order to ascertain the relative accelerating effect of the homologs of aniline and other closely related bases, and also to compare the excess sulfur coefficients with the dissociation constants of the substances originally added as accelerators. The results obtained, together with the physical constants of the substances employed as accelerators, are shown in Table I.

It is evident from this table that with aniline and its methyl derivatives, or in the case of the two phenylenediamines, the substance with the largest dissociation constant produces the greatest excess coefficient of vulcanization. It is also apparent that this relationship is confined to more or less closely related substances only, and that, as a general rule, the dissociation constant is not a reliable guide to the activity of a substance as an accelerator.³

Excess sulfur coefficients of equal magnitude (3.0) were obtained from *p*-toluidine, *p*-benzidine and *m*-phenylenediamine. It is interesting to note that the subtraction of the excess sulfur coefficient of any one of these substances from that obtained for *p*-phenylenediamine (5.2) leaves a figure very close to the excess obtained for aniline (2.4). Further, although the mixtures vulcanized with the assistance of the three substances in question were found to have the same excess sulfur coefficient, all of them had widely differ-

¹ THIS JOURNAL, 12 (1920), 317.

² India Rubber World, 61 (1920), 336.

³ The dissociation constants given in Table I are taken from the Landolt-Börnstein tables and are not strictly comparable, in that they were not all determined by the same method.

TABLE I
First Latex Pale Crepe..... 100
Sulfur..... 8.1
Accelerator..... x
Vulcanized for 90 Min. at 148° C.

SUBSTANCE	FORMULA	x = 0.01 G. Mol.	Determined M. P. or B. P. of Accelerator ¹	Dissociation Constant K at 15° to 18° C	Excess Sulfur Coefficient	—PHYSICAL PROPERTIES—	
						Tensile Strength Lbs. per Sq. In. at Break	Final Length at Break
Control.....					(2.581)	1229	1090
Aniline.....	C ₆ H ₅ NH ₂	0.93	183.1	3.50 × 10 ⁻¹⁹	2.400	2005	910
Methylaniline.....	C ₆ H ₅ NH.CH ₃	1.07	192.0	2.55 × 10 ⁻¹⁹	0.612	1665	1050
Dimethylaniline.....	C ₆ H ₅ N(CH ₃) ₂	1.21	192.5	2.42 × 10 ⁻¹⁹	0.250	1938	1060
p-Toluidine.....	CH ₃ .C ₆ H ₄ .NH ₂	1.07	45.0	1.60 × 10 ⁻⁹	2.987	2476	920
m-Phenylenediamine.....	NH ₂ .C ₆ H ₄ .NH ₂ (1: 3)	1.08	62.6	1.35 × 10 ⁻¹²	2.986	1933	830
p-Phenylenediamine.....	NH ₂ .C ₆ H ₄ .NH ₂ (1: 4)	1.08	140.6	2.48 × 10 ⁻¹²	5.248	193	430
p-Benzidine.....	NH ₂ .C ₆ H ₄ .C ₆ H ₄ .NH ₂	1.84	126.2	7.40 × 10 ⁻¹²	3.056	1464	810
Phenylhydrazine.....	C ₆ H ₅ NH.NH ₂	1.08	240.0	1.60 × 10 ⁻⁹	0.751	1052	1080
Hydrazobenzene ²	C ₆ H ₅ NH.NH.C ₆ H ₅	1.84	126.0		0.777	2165	1140

¹ All m. p. are below, and b. p. above the temperature of vulcanization. ² Figure applies to second "K." ³ Does not have basic properties.

ent physical properties. These substances may be regarded as aniline in which hydrogen of the benzene ring has been replaced by radicals.

On the other hand, (methylaniline), phenylhydrazine, and hydrazobenzene may be regarded as aniline in which the hydrogen of the amino group has been replaced. The difference in the activity of these two types of accelerators has already been mentioned in Part I in connection with the phenylguanidines.

As in the previous instance, the same excess coefficient was obtained for (methylaniline), phenylhydrazine and hydrazobenzene, but the value was much smaller (0.75) than before. The excess value found for these three substances when subtracted from that obtained for p-phenylenediamine gives a figure equal to about twice that obtained with aniline. Here, also, the physical properties of the three mixtures were greatly different.

FIG. 1

The discrepancy in the physical properties of mixtures vulcanized to the same sulfur coefficient by means of different accelerators is of especial interest and has been made the subject of a subsequent paper. As our present results are based on one cure only, we are not warranted in drawing many conclusions from those recorded here. A comparison of the results given in Table I, with the stress-strain curves shown in Fig. 1, however, shows that these differences are most evident at, or near, the point of break.¹

The above results indicate that, irrespective of whether or not an interaction between the accelerator and other substances in the mixture takes place during vulcanization, the activity of substances of

¹ p-Phenylenediamine was so greatly over-cured that concordant results could not be obtained and no curve is given for this substance.

the type described is directly traceable to the amino group, and particularly to the first amino group in the benzene nucleus.

EXPT. II.—In view of the results of Expt. I, they should be analogous to those of ammonia or ammonium salts. From a consideration of the work of Van Heurn¹ it seemed possible that certain other substances, or their reaction products, active as accelerators, might decompose with the formation of a (relatively) strong base and a weak acid in an analogous manner; or that some substances, which are not ordinarily classed as accelerators, owing to their decomposition into a weak base and strong acid, might be active if the acid so formed was neutralized by another constituent of the mixture. Aniline sulfate and p-toluidine hydrochloride, when employed in the presence of zinc oxide, are examples of the latter type.

TABLE II
First Latex Pale Crepe..... 100
Zinc Oxide..... 0
Sulfur..... 8.1
Accelerator..... x
x = 0.01 g. Mol. of Substance
Vulcanized for 90 Min. at 148° C.

MIXTURE	Sulfur Coeffi- cient	Sulfur Coeffi- cient Over Control (+)	Sulfur Coeffi- cient Under Control (-)	PHYSICAL PROPERTIES	
				Tensile Strength Lbs. per Sq. in. (At Break)	Final Length Per cent (At Break)
Rubber-Sulfur Control.....	2.789	...	...	1265	1140
Zinc Oxide Control.....	2.538	...	0.251	...	...
R-S Control + HCl.....	0.652	...	2.137	564	1250
ZnO Control + HCl.....	2.491	...	0.047	1783	820
p-Toluidine.....	5.568	2.779	...	2476	920
p-Toluidine + ZnO.....	5.371	2.833	...	1824	640
p-Toluidine Hydrochloride	2.308	...	0.481	1070	1210
p-Toluidine Hydrochloride + ZnO.....	3.990	1.460	...	2485	757
Methylaniline.....	3.193	0.404	...	1665	1050
Methylaniline + ZnO.....	2.750	0.217	...	2237	800
Methylaniline Hydrochlo- ride.....	1.012	...	1.777	530	1150
Methylaniline Hydrochlo- ride + ZnO.....	2.012	...	0.526	1731	840

In Table II are given the results obtained with molecularly equivalent quantities of p-toluidine and p-toluidine hydrochloride, in the presence and absence of zinc oxide. Two control mixtures were employed, one with and the other without zinc oxide, no accelerator being added in either case. The excess sulfur coefficients (+ or -) shown in the third and fourth columns of this table were obtained by the subtraction of the coefficients of their respective controls, depending upon whether or not they contained zinc oxide.

From this table it is evident that zinc oxide itself exerts a slight retarding action and that hydrochloric acid

¹ Loc. cit.

is a most effectual retardant, when employed in the absence of zinc oxide. When these two substances were both present in the mixture, however, the sulfur coefficient obtained was practically that of its control.

With *p*-toluidine, the same excess coefficient was obtained in the presence and absence of zinc oxide, a characteristic similar to that noted in the case of aniline, and to be discussed in a subsequent paper. In fact, *p*-toluidine hydrochloride did not greatly retard the vulcanization even when employed in a rubber-sulfur mixture, a fact which we attribute to the strong basic nature of the *p*-toluidine. When used in the presence of zinc oxide, *p*-toluidine hydrochloride markedly accelerated the vulcanization. The physical test results confirmed the sulfur coefficients.

Entirely different results were obtained, however, with methylaniline hydrochloride.¹ This substance, although almost inactive in a mixture which contained zinc oxide, acted as a retardant in a mixture of rubber and sulfur only. In this instance, owing to the weakly basic nature of the methylaniline, the effect of the hydrochloric acid predominated. Here, again, the physical properties of the mixtures were roughly in accord with their sulfur coefficients.

The results show that the tendency of certain substances to decompose or dissociate into other substances with acid properties, or with acid properties predominating, may cause the substance originally added to be classed as inactive or as a retardant. In such cases, the primary function of zinc oxide is to neutralize the acidic constituents and permit the predominance of the accelerator, which is very probably basic.

EXPT. III.—Many years ago, Gerard² noted that vulcanization could be effected by boiling rubber in a concentrated aqueous solution of "liver of sulfur," a reaction which may possibly be represented in the following manner:

The second reaction, which represents that found by Gerard capable of effecting vulcanization, is analogous to the decomposition of ammonium polysulfide:

In neither of the above instances is the possibility of the formation of the hydrosulfide (KSH or NH_4SH) excluded, but it is regarded as an intermediate reaction.

In the present case, where the ammonium sulfides³ were used, the resultant system can hardly be acid, no matter how the decomposition or dissociation of the sulfide is effected.

¹ When heated to 350° C., methylaniline hydrochloride dissociates into aniline and methyl halide, with the formation of the isomeric *p*-toluidine. Methylaniline hydrochloride was chosen for comparison with *p*-toluidine hydrochloride, in order to observe if such a rearrangement took place during the vulcanization reaction. From the sulfur coefficients obtained, it is obvious that this transformation did not occur.

² *Loc. cit.* The first use of alkaline sulfides, and particularly potassium pentasulfide, for vulcanization, is often attributed to Gerard (compare Charles Hancock, Brit. Patent 11,874 (1847), and Moulton, Brit. Patent 13,721 (1851)).

³ Compare the process of Moureley of Manchester, England, 1884.

A small sample of the rubber was sheeted thin on the mill and cut into two 5-g. portions. Each portion was placed in a glass bomb tube, and a concentrated aqueous solution of ammonium polysulfide was added to one, and ammonium hydrosulfide to the other. Each solution contained approximately 0.5 g. of sulfide sulfur. The tubes were sealed and heated for 6 hrs. in an oil bath of 147° C.

Both samples appeared to be vulcanized to a slight extent. The sample heated with ammonium polysulfide was dark in color and quite sticky. The other was lighter in color and not so sticky. Both samples were extracted with acetone for 24 hrs., dried, and the combined sulfur estimated.

The samples heated with ammonium polysulfide and ammonium hydrosulfide were found to have sulfur coefficients of 1.933 and 4.366, respectively.

CONCLUSIONS

1—The activity of synthetic nitrogenous organic substances as accelerators is not proportional to the dissociation constants of the original substances and, with the exception of members of a closely related series, no definite relationship exists between the activities and the dissociation constants of the original substances.

2—Substances which decompose or dissociate into other substances of acid character, or react with other components of the mixture to form substances of acid character, do not accelerate unless a neutralizing base or salt is present.

3—Vulcanization is effected by heating rubber in a closed system with concentrated aqueous solution of ammonium sulfides.

ELECTRIC OVEN FOR RAPID MOISTURE TESTS^{1,2}

By Guilford L. Spencer

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The appreciation of the role of the moisture of raw sugars in determining their storage qualities, and the need of very prompt results of moisture tests in sugar-cane bagasse, in controlling the mill work, led the author to devise an oven for rapid tests. The ordinary types of ovens are of great value in these tests, but unfortunately the results in their use cannot be reported with sufficient promptness to meet the needs of thorough factory control. If raw sugar contains more moisture than a certain safety factor indicates is desirable, it may break down before it reaches the market or refiner and serious loss of sucrose result. If the residue of cane milling, the bagasse, contains excessive moisture, this necessitates a waste of fuel and a loss of sugar.

The oven here described is the result of several years' experimenting and the construction of several models. As indicative of the rapidity that has been achieved in the present model, raw sugar may be dried in it in 10 min., and cane bagasse in about 30 min. It was hoped to present comparative tests of several materials and more systematic experiments with sugars.

¹ U. S. Patent 1,348,757.

² Presented before the Section of Sugar Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.