

is considerably increased, and the inlet and outlet gases travel through about 10 ft. of double pipe in counter-current flow. Fine steel wool is used for catalyst.

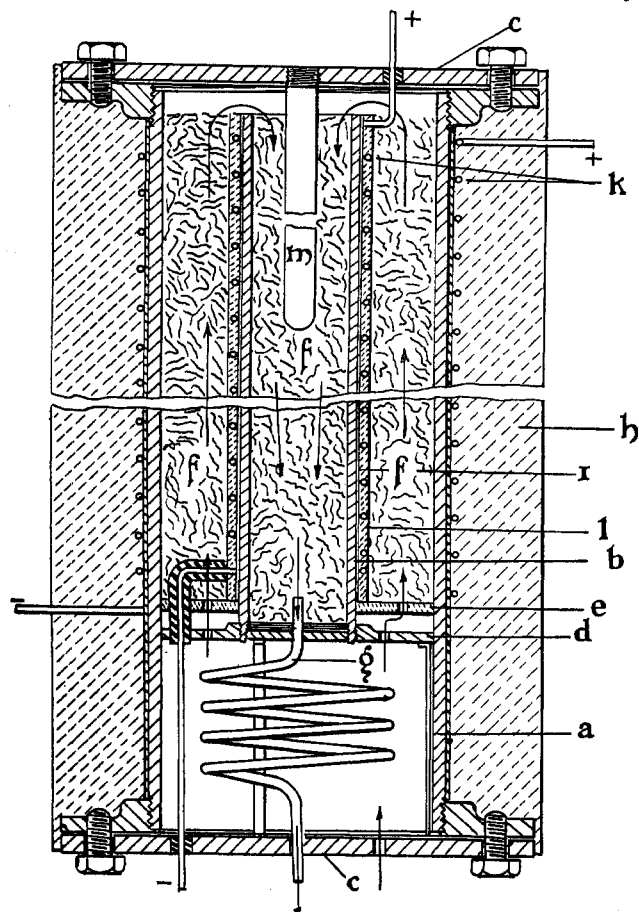


FIG. 3—FURNACE FOR THE DECOMPOSITION OF AMMONIA

- a—5-in. iron pipe
- b—2.5-in. iron pipe
- c—flange ends
- d—flange end to inner pipe
- e—perforated asbestos board
- f—catalyst space
- g—heat interchange coil
- h—insulating material
- i—alundum sheath
- k—resistance coil of chromel wire
- l—alundum cement
- m—pyrometer well

The weight of the furnace is partially supported from above to prevent deformation and the sides and top are covered with 7 in. of infusorial earth.

RESULTS

Table I shows some results obtained in the furnace using iron shavings as catalyst. The flow is measured by the decomposed gas free from NH_3 which passes through the meter.

TABLE I—DECOMPOSITION OF AMMONIA
(Catalyst: Iron. Space: 0.22 Cu. Ft.)

| Temp. ° C. | Flow Cu. Ft. per Min. | Decomposition Per cent |
|---------------|--------------------------|---------------------------|
| 370 | 0.01 | 73.0 |
| 470 | 0.15 | 84.0 |
| 540 | 0.01 | 94.0 |
| 600 | 0.20 | 97.0 |
| 600 | 2.00 | 94.5 |
| 610 | 0.50 | 93.5 |
| 650 | 0.62 | 99.6 |
| 650 | 1.50 | 97.4 |
| 675 | 0.50 | 99.7 |
| 675 | 1.00 | 99.5 |
| 700 | 1.50 | 99.7 |
| 710 | 2.00 | 99.6 |
| 735 | 0.82 | 99.7 |

For ordinary operation a temperature of 675° C. is maintained which enables one to obtain about 100 cu. ft. per hr. of the hydrogen-nitrogen gas mixture with a power consumption of 2 k. v. a. with loss

of 0.3 to 0.4 per cent of ammonia. The equilibrium of a system of H_2 - N_2 - NH_3 at that temperature and atmospheric pressure theoretically should be about 0.02 per cent NH_3 . The average time of contact in the catalyst space is about 5 sec. This time could probably be reduced considerably.

A small preliminary furnace in which copper chips and turnings were used for catalyst was employed before this one was constructed. Table II shows results obtained with this.

TABLE II—DECOMPOSITION OF AMMONIA
(Catalyst: Copper. Space: 0.11 Cu. Ft.)

| Temp. ° C. | Flow Cu. Ft. per Min. | Decomposition Per cent |
|---------------|--------------------------|---------------------------|
| 750 | 0.01 | 96.0 |
| 750 | 0.25 | 75.0 |
| 800 | 0.05 | 97.3 |
| 850 | 0.01 | 99.7 |
| 850 | 0.22 | 99.4 |
| 850 | 0.95 | 90.5 |
| 900 | 0.85 | 96.2 |
| 925 | 0.50 | 99.3 |
| 925 | 1.00 | 97.5 |

It will be seen that copper requires a temperature about 200° C. higher than iron, and a longer contact. The figures are not strictly comparable for the iron surface was probably of the order of ten times that of the copper. Beilby and Henderson¹ emphasize the fact that ammonia decomposes less rapidly in contact with copper than with iron.

Because of the lower operating temperature and cheapness, iron was chosen in preference to copper as a catalyst.

The furnace with steel shavings was in operation for about 6 mo. when the outer coil burned out. On taking apart the iron, shavings were found to have sintered into a compact mass and to be attached firmly to the sides of the iron pipe. The pipe itself, which had operated continuously in an atmosphere of hydrogen and nitrogen, showed attack from within to such a degree that it was granular and cracked about two-thirds the distance through the wall (0.25 in. thick) and crystallized the other third. The metal was very brittle and the pipe was readily broken up with a hammer. Beilby and Henderson² and Henderson and Galletly³ found a similar deterioration of metals exposed to ammonia at high temperatures. Probably this was due to the formation of iron nitride or hydride, or both. The nichrome wire used as resistance winding seemed to be in as good condition as when first wound. The maximum temperature to which the furnace had been subjected was not over 900° C., and this temperature was reached inadvertently and maintained for a very short time.

THE ACTION OF CERTAIN ORGANIC ACCELERATORS IN THE VULCANIZATION OF RUBBER⁴

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Since the introduction of the use of organic substances to assist in, or to accelerate, the vulcanization

¹ *J. Chem. Soc.*, **79** (1901), 1245.

² *Loc. cit.*

³ *J. Soc. Chem. Ind.*, **27** (1908), 387.

⁴ Presented before the Rubber Division at the 58th Meeting of the American Chemical Society, Philadelphia, Pa., September 2 to 6, 1919.

of rubber, there has been remarkably little added to the literature upon the subject. Furthermore, what has been written has been confined largely to reviews of a general nature. Although King,¹ Peachey,² Twiss,³ Spence,⁴ and others⁵ have contributed to this subject, the majority of investigators have remained reticent, despite the fact that the patent files are replete with information.

The present paper records a portion of the results procured in an attempt to obtain further information in regard to the action of certain organic substances in accelerating the vulcanization reaction. Throughout this work we have chosen to employ only substances which have previously been cited by others and whose definite chemical composition permits comparison with homologs or other closely related compounds. The activities of the substances from a practical standpoint were considered of secondary importance. Further, while we most assuredly recognize that the vulcanization reaction is, essentially, a catalytic one, we have chosen to employ the term "accelerator" rather than "catalyst," when referring to the organic substances in question. This distinction is deemed necessary to avoid misunderstanding, and to discriminate between catalysis as it is generally understood and as it must be applied to the vulcanization of rubber. In this regard, it is necessary to take into consideration the fact that a large number of the organic substances used to accelerate the vulcanization of rubber decompose below the temperatures at which vulcanization is ordinarily effected, and that many of them show a tendency to combine with the sulfur under vulcanizing conditions. Again, as most of the rubber mixtures in actual use contain mineral substances, the possibility of a reaction of these substances with the organic accelerators involving the alteration or decomposition of the latter, is far from remote. In fact, even before the general use of synthetic organic substances as accelerators, Esch⁶ found it necessary to employ calcium and magnesium oxides with certain albuminous bodies in order to obtain the desired results. Likewise, Peachey⁷ has noted a marked increase in the activity of *p*-nitrosodimethylaniline when used in conjunction with magnesia. Litharge was found to diminish the effectiveness of this accelerator.

Although we are confident that the use of organic substances as accelerators was practiced in the factories of this country long before the first patent on the subject was taken out abroad, the predominance of the early patents was undoubtedly German. In fact, the latter people, with their thoroughness and the realization of the possibilities in the subject, attempted to restrict the use of all nitrogenous substances by the use of such generalities as are found in one of Bayer

and Company's patents.¹ That few, if any, applications for license to use these patents were made during the war is an indication of our priority in this field.

The first German patents upon accelerators appeared almost coincidentally with certain patents for the preparation of synthetic rubber, when it was found that this substance was abnormally slow in its reaction with sulfur. In this connection, Bayer and Company found that piperidine or its homologs² and the piperidine salt of piperidyl-dithiocarbamic acid³ effected a marked acceleration in the vulcanization of Kondakow's rubber,⁴ and, subsequently, they extended their claims to cover natural rubber. Prior to the above Bayer patents, however, a patent was issued to Wo. and Walther Ostwald⁵ for the treatment of rubber, gutta-percha, and the like, with pyridine, quinoline, dimethylaniline, etc., in order to prevent its becoming hard and fragile. It is most remarkable that in the course of this work the Ostwalds failed to note the action of certain salts of these and other closely related substances in accelerating the vulcanization of the rubber, even though the parent substances themselves possess little, if any, action.

Immediately following the patents for the use of piperidine and its derivatives appeared a variety of specifications covering the use of dimethylamine,⁶ aldehyde ammonia, tetra- and hexamethylenediamines, *p*-phenylenediamine, and naphthylenediamines;⁷ the formaldehyde condensation products of aniline and its homologs;⁸ the guanidines;⁹ naphthylamine;¹⁰ and a large number of other amino-compounds, or nitrogenous substances, all of which have been mentioned previously by King, Peachey, Twiss, Spence, or Ditmar, and include such substances as quinoline and its salts, the quaternary ammonium bases, urea and thiourea derivatives, and a host of others. In their patents, Bayer and Company cover the urea and thiourea derivatives of saturated aliphatic amines, both open and closed carbon chains, which are saturated methylene open-carbon chain bases. The term "methylene base" is held to be generic to those bases which are saturated bases as distinguished from unsaturated bases as aniline. Suffice to say, that both aniline and diphenylthiourea were employed in this country long before the appearance of any of the above specifications.¹¹

Although not specified in some of the foregoing patents, many of these were drawn upon the assumption that the activities of the various substances depended

¹ *Met. & Chem. Eng.*, **15** (1916), 231; **18** (1918), 246.
² *India Rubber J.*, **52** (1916), 603; *J. Soc. Chem. Ind.*, **36** (1917), 321; **36** (1917), 424, 950.
³ *J. Soc. Chem. Ind.*, **36** (1917), 782.
⁴ *THIS JOURNAL*, **10** (1918), 115.
⁵ *Gummi Ztg.*, **29** (1915), 425; **30** (1916), 303; *India Rubber World*, **55** (1917), 190; *Caoutchouc et gutta-percha*, **15** (1918), 9637; *Rubber Age*, **3** (1918), 78.
⁶ D. R. P. 273,482 (1912).
⁷ *J. Soc. Chem. Ind.*, **36** (1917), 424.

¹ D. R. P. 280,198 (1914).

² D. R. P. 255,680, 266,618 (1912); 268,387, 265,221 (1912).

³ D. R. P. 266,619 (1912); U. S. Patent 1,126,469 (1915).

⁴ *J. prakt. Chem.*, **64** (1901), 109.

⁵ D. R. P. 221,310 (1908).

⁶ D. R. P. 269,512; French Patent 464,533.

⁷ D. R. P. 280,198 (1914); U. S. Patent 1,149,580 (1915).

⁸ British Patent 7,370 (1914).

⁹ British Patent 17,760 (1916).

¹⁰ U. S. Patent 1,296,469 (1919).

¹¹ In this connection it is interesting to note that in this country attention was directed to the use of urea as an accelerator before the appearance of these or any other patents upon urea or the thiouréas. This is said to have been the result of observations made upon certain African rubbers, reputed to have been coagulated with human urine, and which were found to vulcanize with more than average rapidity.

largely upon their nitrogenous nature and the basicity of the substances in question.

In view of the well-known effect of such inorganic bases as caustic soda or potash upon the vulcanization of rubber, the opinion that the basicity of certain substances is closely connected with their action as accelerators has found quite a few adherents. Among these is Twiss,¹ who believes that both the organic and inorganic accelerators, all of basic nature, exert their influence in a similar manner. According to Twiss, the more powerful action of the organic bases is due to their greater solubility in the rubber, a principle which he has applied in preparing very active accelerators by the use of an organic liquid which would be soluble in the rubber and also act as a solvent for alkali. In a subsequent patent² he has still further extended this view to include such materials as solutions of sodium and potassium in aniline, the action of which would be difficult indeed to classify if essential differences are held to exist between the action of organic and inorganic accelerators. Peachey,³ however, in his patent upon *p*-nitrosodimethylaniline, has taken another view, and attributes the activity of this substance, primarily, to the presence of the nitroso group. Subsequently, Peachey⁴ has also expressed the opinion that, while the dissociation constant of 1×10^{-8} , referred to in the Bayer patents, does actually form a dividing line between accelerating and non-accelerating bases, there are other classes of accelerators (as *p*-nitrosodimethylaniline) which are not basic, or but slightly so. Further, in order to emphasize not only the effect of certain groups, but also the position of these groups in the molecule, Peachey has cited the nitroso bases as powerful accelerators, and pointed out that the isomeric nitrosamines, in which the nitroso group is not in direct combination with the nucleus, are inert.

Likewise, Spence has mentioned that the activity of certain substances which contain groups in the para position are more active than the isomeric substances, in which the groups are in the ortho, or meta position, and has cited the relative activities of *p*-phenetidine and *o*-phenetidine as an example. He has also called attention to the increase effected in the activity of substances as accelerators by the introduction of other groups into the nucleus. As a case in point, he has made reference to the increase in the activity of diphenylthiourea when it is converted into tetramethyldiaminodiphenylthiourea. While there is no doubt that these differences exist as expressed by Peachey and Spence, it is to be regretted that no figures were given by either of them by which the relative activities of the various substances might be recorded.

Our own experience, a portion of which is embodied in the experimental part of this paper, in the main confirms the results of Peachey and Spence; and in fact, in many ways, permits of their amplifications.

¹ *J. Soc. Chem. Ind.*, **36** (1917), 782; British Patent 110,059 (1916).

² British Patent 124,276 (1919).

³ British Patent 4,263 (1914).

⁴ *J. Soc. Chem. Ind.*, **36** (1917), 950.

Not only have we found certain groups, and the position of these groups in the primary nucleus, to have a marked effect upon the activity of the substance under investigation, but we have found that if the effect produced by one or more groups is to be considered on a strictly comparable basis, the size (molecular weight) of the parent substance must also be taken into account. On the other hand, we are equally well convinced that with many substances it is possible to place too great stress upon the presence of certain groups and their position in the nucleus. It would appear that the effect produced by the different groups is largely determined by their behavior and ultimate condition as the original substance undergoes decomposition or chemical change, and that the activity of substances not originally basic is due to their conversion into basic substances during vulcanization.

For example, in our preliminary experiments we found that urea was slightly more active than thiourea. Thiourea, in turn, was more active than monophenylthiourea, and the latter more active than diphenylthiourea. The same was true in the case of the guanidines, both monophenylguanidine and diphenylguanidine being found more active than triphenylguanidine, although the conditions of our experiment did not permit of a differentiation between the two substances first mentioned. In the case of the thiourea, the natural inferences would be that the activity of the parent substance depended largely upon the presence of the NH_2 groups, with a consequent diminution in the effect produced as phenyl replaces hydrogen. In the case of the guanidines, the great difference in activities of mono- and diphenylguanidines, when compared with that of triphenylguanidine, may be attributed to the fact that in the latter substance the phenyl group has replaced imido rather than amido hydrogen.

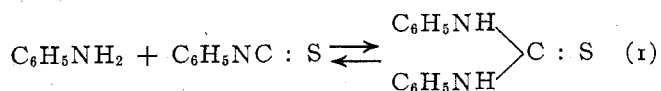
Again, when we made a comparison between a cyclic monamine and diamine, we found the latter, in accordance with the now general understanding, to be much more active than the former, if the groups are in the para position. On the formation of the anhydro-formaldehyde condensation products of these substances, however, although the activities of each were increased by the substitution of methylene groups for the hydrogen of the amino groups in the original substances, this increase in the case of the monamine was much less than that produced by the introduction of a second amino group into the original nucleus. Although the two types of compounds are not isomeric, this is in line with Peachey's statement as to the effect produced when groups are introduced into a side-chain rather than the original nucleus.

In our subsequent and more extensive experiments, wherein we employed aniline as a basis of comparison, we found that the replacement of the amino group in aniline by hydroxyl actually decreased the rate of vulcanization to less than that of the control mixture which contained no accelerator. The introduction of a second hydroxyl group in the para position was found to cause a still greater retardation in the rate of re-

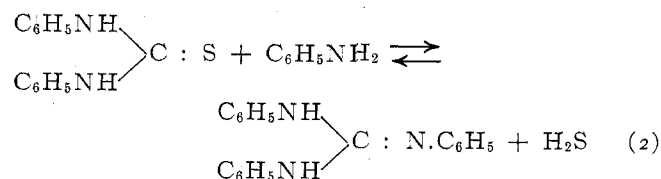
action. In fact, when allowance was made for the difference in the molecular weights of the two substances, the anti-accelerating effect of hydroquinone was found to be just twice that of phenol. The difference between the effect of one amino group and two amino groups in the para position has already been mentioned, and here again, after having corrected for the molecular weights of the two substances, *p*-phenylenediamine was found to be almost exactly twice as active as aniline. When we employed *p*-amidophenol, however, in order to obtain an amino group and an hydroxyl group in the para position to each other, our results were not strictly in accordance with those of Peachey and Spence, who found that this substance was without action or but mildly active. On the contrary, we found *p*-amidophenol to be more active than aniline. The inference from our results would be that although the effect of the (OH) group is that of a retardant, its position in the nucleus, and its subsequent influence upon the decomposition of the nucleus during vulcanization, are of less importance than the effect produced by the stronger and positive (NH₂) group.

It is not our purpose, however, to attribute the action of certain substances as accelerators entirely to the inclusion and position of certain groups in the primary nucleus. Rather, as has been said, we have been led to the conclusion that the great majority of organic accelerators owe their activity to their decomposition products, when this decomposition takes place in the presence of sulfur and under vulcanizing conditions. This corresponds very closely with Spence's third class of accelerators, which he believes may be inactive in themselves, but which, at the temperature of vulcanization, either alone or in the presence of other substances, may break down into a substance, or substances, having the properties of powerful catalysts. He has mentioned diphenylthiourea as an example of this type.

In the final experiment recorded in this paper, we have worked along these lines with aniline as a standard and have compared its activity with that of other substances into which it can be converted, or from which it can be derived by decomposition under vulcanizing conditions. The following reaction suffices to explain our method:



That such a reaction, from right to left, actually takes place was indicated when we found that a mixture vulcanized with the assistance of a certain definite amount of diphenylthiourea had the same sulfur coefficient as that of a similar mixture, vulcanized under the same conditions, to which had been added aniline and phenyl mustard oil, in accordance with the amounts required by Equation 1. Similar sulfur coefficients also resulted for two mixtures, one of which was vulcanized with the assistance of triphenylguanidine and the other with quantities of diphenylthiourea and aniline, in accordance with Equation 2.



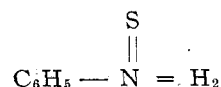
The above reaction, likewise, takes place from right to left. The diphenylthiourea and aniline formed, however, evidently undergo further decomposition with the formation of two molecules of aniline and one molecule of phenyl mustard oil.

Our interpretation of these results led us to the conclusion that both diphenylthiourea and triphenylguanidine owe their powers of acceleration to their tendency to decompose with the formation of aniline. On the other hand, and in view of our results as a whole and particularly those obtained with urea and thio-urea, we certainly do not feel warranted in ascribing to aniline alone those properties which Spence has termed the "active principle." Rather, we are inclined to regard aniline as one of the simpler substances that contains a group which, under vulcanizing conditions and temperatures, functions as a sulfur carrier.

To elaborate upon the action of accelerators beyond this point, however, is hardly warranted from the results obtained. Moreover, further discussion must, necessarily, involve the theory of vulcanization in its entirety, which is not our intention in this communication.

We have shown that under vulcanizing conditions and temperatures, certain accelerators decompose or suffer degradation to simpler substances which are responsible for the acceleration effected. The decomposition of diphenylthiourea to aniline is an example. Such being the case, similar decompositions would appear possible with other substances. This decomposition having been effected, the action of the decomposition or alteration products is most conveniently interpreted on the basis of a change in the valency of the nitrogen in active groups from 3 to 5.

It is not to be understood, however, that we believe aniline as such is, necessarily and quantitatively, formed by the decomposition of diphenylthiourea under vulcanizing conditions. Further, the various complexes which we have postulated for aniline, *p*-phenylenediamine, etc., serve to account only for the relationship noted between the activity of the substance in question and its nitrogen content. Theoretical deductions of a general nature are not at present possible, as results obtained by Erdmann¹ and Ostromyslenskii² indicate that the active sulfur may take the form of a polysulfide and may even not be attached to nitrogen. However, for the purpose of interpretation, rather than deduction, and with aniline as an example, under the conditions and temperatures at which vulcanization takes place, we postulate the existence of the following complex:

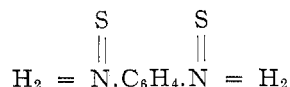


¹ *Ann.*, **362** (1908), 133.

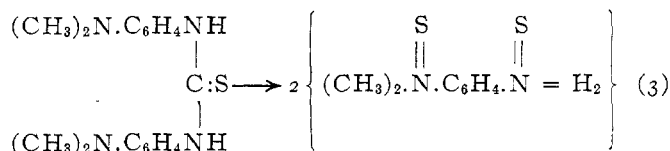
² A. H. King, *Mel. & Chem. Eng.*, **18** (1918), 245.

As this complex would not be stable, except under the conditions and temperatures at which vulcanization is effected, it would function as a catalytic sulfur carrier, releasing its sulfur in an active form, which would combine with the rubber more readily than the sulfur originally included in the mixture. Its catalytic action would depend upon its ability to maintain an equilibrium between the active and inactive sulfur.

The above is in strict accord with our results for the relative activity of aniline and *p*-phenylenediamine. The hypothetical complex for the latter substance would include 2 pentavalent nitrogen atoms, or active groups, as below:



Thus, when the effect of molecularly equivalent quantities of aniline and *p*-phenylenediamine are compared, the latter should be just twice as active as the former. This was actually found to be the case. From this it is also possible to explain why Spence found tetramethyldiaminodiphenylthiourea so much more active than diphenylthiourea; the former substance would probably decompose into 2 molecules of dimethyl-*p*-phenylenediamine with just twice the number of active groups found in the latter. Further, we venture to predict that the activity of one molecular part of tetramethyldiaminodiphenylthiourea is exactly equal to that of 2 equimolecular parts of dimethyl-*p*-phenylenediamine,¹ and less than that of 2 equimolecular parts of *p*-phenylenediamine. The difference in the basicities of the last two substances accounts for their relative activities



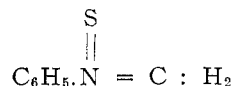
The latter observation is made in the light of our results with the ureas and guanidines. While our results with these substances are subject to the same general interpretation as the preceding, we found with them that the replacement of the hydrogen by phenyl in the active groups decreased the activity of the substance in question. It is possible that the substitution of larger groups for the hydrogen attached to the active nitrogen would cause the group to become inactive, due to steric hindrance precluding the formation of pentavalent nitrogen. Peachey's observation of the inactivity of the nitrosamine isomeric with *p*-nitrosodimethylaniline may be subject to this interpretation.

In view of this, our results with the anhydro-formaldehyde condensation products of aromatic

¹ It is interesting to note that Eaton, Grantham and Day (Dept. of Agr. Fed. Malay States, *Bulletin* 27 (1918), 319) found dimethyl-*p*-phenylenediamine hydrochloride to exert a marked retarding influence upon the vulcanization of a fast curing rubber. In this case, then, the nitrogen of the amino group is already pentavalent, and could not act as a sulfur carrier; it has already been shown that acid groups act as retardants.

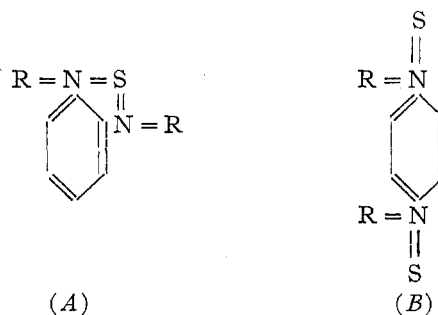
In this connection, it should also be pointed out that although dimethyl-*p*-phenylenediamine is more active than aniline, dimethylaniline is practically inert.

amines are more difficult to interpret, as the substitution of methylene for hydrogen increased the activity. In this instance, however, there will be two double bonds when nitrogen becomes pentavalent:



A complex of this type would be even more unstable, and more active, than that postulated for aniline.¹

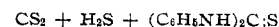
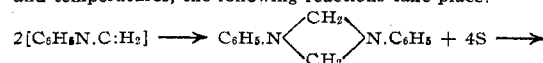
Lastly, in light of the readiness with which sulfur passes from the di- to the tetra- or hexavalent state, it is possible to adapt the former principles to account for the difference in the relative activities of the *o*- and *p*- products of the same substance. The proximity of two groups in the *o*-position might lead to a complex of type A, whereas, if the groups were in the *p*-position, the configuration would be that shown in type B.



In this case, then, the *p*- would be twice as active as the *o*-product, a condition with which we are not as yet familiar.

In the foregoing we have not taken into consideration the effect of the accelerators upon the physical properties of the mixtures investigated, and have confined our remarks to interpretations made on the basis of excess sulfur coefficients of vulcanization only. However, in our experiments with mixtures vulcanized with the assistance of aniline, diphenylthiourea and triphenylguanidine, we were able in no instance to recover the original amount of the accelerator in the acetone extract. While this does not permit us to state definitely that a portion of the accelerator or its decomposition products, as well as the sulfur, becomes closely bound to the rubber molecule, it is not impossible that such is the case. We agree with King, that the remarkable improvement imparted to mixtures vulcanized with the assistance of certain organic accelerators indicates that the binding between the

¹ In the paper by C. W. Bedford and W. Scott, read immediately after the above, the following explanation was offered for the behavior of this substance. According to the above authors, under vulcanizing conditions and temperatures, the following reactions take place:



We have already shown that diphenylthiourea probably decomposes into aniline and phenyl mustard oil. Further, we have shown that when compared on equal weights the activities of anhydro-formaldehyde aniline and diphenylthiourea are approximately the same. As the molecular weight of diphenylthiourea is over twice that of anhydro-formaldehyde aniline, and as two molecules of the latter and one molecule of the former would each decompose into one molecule of aniline, a comparison with equal weight of the two substances should show anhydro-formaldehyde aniline to be slightly more active than diphenylthiourea. This is in strict accordance with the above reactions and our findings.

"active principle," or active group, of certain of the organic accelerators and the rubber is a close one.

In the course of another investigation shortly to be published, we have shown that fundamental differences exist between vulcanized mixtures of rubber and sulfur, and similar mixtures vulcanized with the assistance of an organic accelerator. This is subject to still further modification if either type of mixture contains a mineral oxide.

EXPERIMENTAL PART

The same general method of procedure was pursued in this work as in that previously reported.

The rubber used was good quality, first latex, pale crêpe, and the same lot was employed in all mixtures. All mixtures were made under standard conditions; the average time of each batch on the mill was 17.5 min. The same proportion of rubber and sulfur—92.5 parts rubber, and 7.5 parts sulfur—was employed in each instance, but the amount of accelerator was varied, according to the conditions of the experiment.

All of the accelerators soluble in alcohol were dissolved in the smallest quantity of this liquid and introduced into the rubber in solution. Those not soluble—and this applied to the anhydro-formaldehyde bodies only—were ground to 100 mesh and added to the rubber with the sulfur. After mixing, the mixtures were allowed a recovery period of 24 hrs. before they were vulcanized. Vulcanization was carried on in a platen press of the usual type.

The vulcanized sample for analysis was then sheeted thin on the mill, subjected to 24 hrs. continuous extraction with acetone in the extractor recommended by the Joint Rubber Insulation Committee,¹ dried in air and *in vacuo* at 100° C. to constant weight. The free, or extractable, sulfur found in the acetone extract was estimated by the bromine oxidation method of the Bureau of Standards.² The combined sulfur in the extracted rubber was estimated by a method of our own, to be reported upon in the near future.³ All figures given for per cent sulfur are the average of at least 2 determinations which checked to within 0.1 per cent.

PRELIMINARY EXPERIMENTS—With the exception of aniline, which was purified by distillation and boiled at 185° C., all of the accelerators shown in Table I were recrystallized from alcohol. The purified products were found to have the following melting points: urea, 132° C.; thiourea, 168° C.; monophenylthiourea, 153° C.; diphenylthiourea, 151° C.; monophenylguanidine, 193° C.; *sym*-diphenylguanidine, 147° C.; triphenylguanidine, 143° C.

In the case of the substances shown in Table II, the *p*-phenylenediamine was recrystallized from alcohol and melted at 146° C. The anhydro-formaldehyde bodies possessed the following melting points: anhydro-formaldehyde aniline, 140° C. (with decomposition); monoanhydro-formaldehyde *p*-phenylene-

diamine, 142° C.; dianhydro-formaldehyde *p*-phenylenediamine, 192° C.

TABLE I—RELATIVE ACTIVITIES—THIOUREA SERIES
Parts Required to Equal One Part Aniline

| | |
|---------------------------------------|-------|
| Aniline..... | 1.000 |
| Urea..... | 0.250 |
| Thiourea..... | 0.300 |
| Monophenylthiourea..... | 0.450 |
| Diphenylthiourea..... | 0.850 |
| Monophenylguanidine (α)..... | 0.075 |
| Diphenylguanidine (<i>Sym</i>)..... | 0.075 |
| Triphenylguanidine..... | 0.500 |

The activities of the various substances were compared in the mixture previously mentioned—92.5 parts of rubber and 7.5 parts of sulfur—taking as a standard¹ the effect obtained with one part of aniline, vulcanized for 90 min. at 148° C. The amounts of various substances in the urea series required to effect the same degree of vulcanization as obtained with one part of aniline are shown in Table I. The same is true for the anhydro-formaldehyde aniline series, the results of which are shown in Table II.

TABLE II—RELATIVE ACTIVITIES—ANHYDRO-FORMALDEHYDE SERIES
Parts Required to Equal One Part Aniline

| | |
|--|------|
| Aniline..... | 1.00 |
| Anhydro-formaldehyde aniline..... | 0.75 |
| <i>p</i> -Phenylenediamine..... | 0.17 |
| Monoanhydro-formaldehyde <i>p</i> -phenylenediamine..... | 0.14 |
| Dianhydro-formaldehyde <i>p</i> -phenylenediamine..... | 0.14 |

As these preliminary tests were conducted solely to obtain information for guidance in subsequent experiments, and as no sulfur estimations were made, we do not feel warranted in drawing extensive conclusions from them. It would appear, however, that in the case of the urea series, the introduction of phenyl as a substituent for the hydrogen of the amido or imido group is responsible for a marked decrease in the activity of the parent substance. Also, in the case of the anhydro-formaldehyde series, it is evident that the introduction of the second amino group into the benzene nucleus increases the activity of the substance to a greater extent than substituting methylene for the hydrogen in the original amino group.

FINAL EXPERIMENTS—(1) This experiment was carried out in order to determine the relative accelerating effects produced by certain substances which contained hydroxyl or amino groups in their primary nucleus. Determinations were also made of the effect produced when the number, or kinds, of groups in the nucleus were altered or changed.

Every effort was made to obtain the various substances in the greatest degree of purity. Their physical constants were as follows: phenol, m. p. 41° C.; *p*-amidophenol, sublimed at about 180° C.; aniline, b. p. 185° C.; hydroquinone, m. p. 168° C.; *p*-phenylenediamine, m. p. 146° C.

The relative activity of these substances, as expressed by their sulfur coefficients, is shown in Table III.

¹ The comparisons were made at what was judged to be in each case the correct cure, as measured by the physical properties of the various mixtures only. Owing to this fact, the values assigned in Tables I and II were not found to be in strict agreement with their respective sulfur coefficients as determined in the subsequent experiments. Such comparisons, based on physical properties alone, are apt to be misleading, due to the toughening action imparted to the rubber when certain accelerators are employed; this effect is very noticeable in the case of *p*-phenylenediamine.

¹ THIS JOURNAL, 6 (1914), 514.

² Bureau of Standards, Circular 38 (1915), 66.

³ This method was evolved and applied in the course of the present work, in order to overcome certain disadvantages in the Rosenstein-Davies method (*Chemist-Analyst*, 15 (1915), 4) previously employed.

TABLE III—RELATIVE ACCELERATION
 First Latex Pale Crêpe..... 92.5 parts
 Sulfur..... 7.5 parts
 Accelerator..... 1 part
 Vulcanized for 90 min. at 148° C.

| ADDED SUBSTANCE | Combined Sulfur Per cent | Sulfur Coefficient | Excess Sulfur Coefficient | Group Coefficient |
|--|--------------------------|--------------------|---------------------------|-------------------|
| Control..... | 1.792 | 1.937 | | |
| Phenol..... | 1.629 | 1.779 | —0.158 | —0.00168 |
| Hydroquinone..... | 1.430 | 1.561 | —0.376 | —0.00170 |
| <i>p</i> -Amidophenol..... | 4.772 | 5.210 | + 3.273 | ... |
| Aniline..... | 4.226 | 4.614 | + 2.677 | + 0.02870 |
| <i>p</i> -Phenylenediamine ¹ .. | 7.286 | 7.955 | + 6.018 | + 0.02780 |

¹ As the combined sulfur obtained in this instance is so close to the total amount originally added to the mixture, this comparison was repeated with 0.25 per cent aniline and *p*-phenylenediamine. When employed in this amount, aniline gave an excess sulfur coefficient of 1.421 and *p*-phenylenediamine, 3.552. On calculation, their group coefficients were found to be 0.01530 and 0.01640, respectively.

From this table, it is seen that phenol, when expressed in terms of its sulfur coefficient, has a slight retarding influence which is almost exactly doubled in the case of hydroquinone, when the molecular weight of the latter is taken into consideration. Aniline and *p*-phenylenediamine are seen to exert a marked accelerating effect, as would be expected, and here, again, the effect produced by two amino groups is almost exactly twice that of a single group when the molecular weights of the two substances (aniline and *p*-phenylenediamine) are taken into consideration.¹ Thus, when equal weights of certain accelerators which contain active groups in the same primary nucleus are employed, it is possible to compare the activity of these groups *per se* by means of a group coefficient. Or, conversely, molecular quantities of substances which contain the same active group (or groups, if in equal number) in the primary nucleus should produce the same accelerating activity.

In the case of equal quantities by weight, this may be expressed as follows:

$$\text{Group coefficient} = \frac{Sx}{Mn}$$

where Sx = the excess sulfur coefficient over that of a control mixture vulcanized without an accelerator.

M = the molecular weight of the accelerator.

n = the number of the groups in the primary nucleus.²

When the results recorded in Table III are substituted in the above expression, the coefficient for the (OH) group is seen to be in good agreement for both phenol and hydroquinone; the same is true for the coefficients obtained for the (NH₂) group in both aniline and *p*-phenylenediamine. In other words, the introduction of a second group in the para position just doubles the activity. In light of our remarks in the introductory part of this paper, in regard to the function of these groups in accelerating the reaction between rubber and sulfur, we regard this point of

¹ The alkaloidal substances mentioned by Spence as decidedly active are undoubtedly of a high molecular weight.

² The term "nucleus" is used as distinct from "molecule," in order to preclude the inclusion of similar groups in the side chains which, as Peachey has already noted, are not comparable in the effect produced. Likewise, as our work has been confined to two groups in the para position, further extension of this principle would require the introduction of another factor to compensate for the appearance of groups in the meta and ortho positions. In the most cases, the ortho, meta and para products are increasingly active in the order named. Such differentiations, however, may be carried on indefinitely to include naphthylamines, etc. We have found β -naphthylamine to be almost twice as active as α -naphthylamine.

much more importance than the numerical coefficient of the group itself, although a properly arranged table of group coefficients would undoubtedly be of value in anticipating the activities of untried substances.

II—In the previous experiment we employed substances of comparatively simple composition, and have attributed their action as accelerators to the presence of certain active groups. In the introductory part of this paper, however, we have pointed out that the action of certain other accelerators depends upon their ability to decompose, under vulcanizing conditions and temperatures, into degradation products containing an active group which is responsible for the acceleration effected. The present experiment was designed to further emphasize this point.

For this purpose, diphenylthiourea was chosen as the standard accelerator, on the assumption that Equation 1 is reversible and proceeds from right to left under the conditions and temperatures at which vulcanization ordinarily takes place.

Such being the case, and in view of the probable inactivity of phenyl mustard oil, the activity exerted by one part of diphenylthiourea should be no greater than that effected by a quantity of aniline corresponding to the amount required for the above reaction, when it is proceeding towards the left. Likewise, if the accelerating effect obtained with diphenylthiourea is dependent solely upon the amount of aniline formed by the decomposition of the former substance during vulcanization, the same should be true for triphenylguanidine, in accordance with Equation 2, which should also proceed from right to left during the vulcanization.

As mentioned in the introductory part of this paper, the diphenylthiourea and aniline formed undoubtedly undergo a subsequent decomposition with the formation of 2 molecules of aniline, and 1 molecule of phenyl mustard oil.

In order to test the above, our standard mixture was vulcanized for 90 min. at 148° C., with the assistance of one part of diphenylthiourea, and compared with similar mixtures which contained molecularly equivalent amounts of either one or both of the various decomposition products indicated in the above equations. The actual amounts of the different substances employed are shown in the second column of Table IV; they showed the following physical constants: phenyl mustard oil, b. p. 220° C.; aniline, 185° C.; diphenylthiourea, m. p. 151° C.; triphenylguanidine, m. p., 143° C.

Before any sulfur determinations were made, the different slabs were submitted to thumb and tooth tests in order that a rough estimation of their relative physical properties might be recorded. As shown in Table IV, the control has been used as the standard for comparison and given the number 1. The value 2, given to diphenylthiourea, simply indicates that it was faster than 1; number 3 was considered faster than 2, and so on for the rest of the series. The differences existing between the physical properties of the various slabs, however, were in no sense proportional to the numbers given them. The odor of the cured slabs was recorded in each instance and found to substantiate

TABLE IV
First Latex Pale Crêpe..... 92.5 parts
Sulfur..... 7.5 parts
Accelerator..... X parts
Vulcanized for 90 min. at 148° C.

| | X = Parts Accelerator Added to the Mixture | Physical Prop- erties | ODOR OF CURED SLAB | —Acetone Extract— Per cent (Uncor- rected) | Per cent (Cor- rected) | Free Sulfur Per cent | Com- bined Sulfur Per cent | Total Sulfur Per cent (By Ad- dition) |
|----------------------------------|---|-----------------------------|---|--|---------------------------|----------------------------|-------------------------------------|---|
| Control..... | 0.00 | 1 | Standard | 8.630 | 2.894 | 5.736 | 1.792 | 7.528 |
| Phenyl Mustard Oil..... | 0.59 | —1 | Phenyl mustard oil | 8.443 | 2.729 | 5.714 | 1.726 | 7.440 |
| Aniline..... | 0.41 | 4 | Decomposition products of aniline | 7.065 | 3.137 | 3.928 | 3.625 | 7.553 |
| Phenyl Mustard Oil and Aniline | $C_6H_5NCS = 0.59$ $C_6H_5NH_2 = 0.41$ | 3 | Phenyl mustard oil and decomposition prod- ucts of aniline, the latter predominating | 7.966 | 3.595 | 4.371 | 3.100 | 7.471 |
| Diphenylthiourea | 1.0 | 2 | Phenyl mustard oil and decomposition prod- ucts of aniline, the latter predominating | 7.429 | 3.119 | 4.310 | 3.078 | 7.388 |
| Diphenylthiourea and Aniline.... | $(C_6H_5NH)_2CS = 1.0$ $C_6H_5NH_2 = 0.41$ | 6 | Decomposition products of aniline predom- inating | 7.301 | 3.963 | 3.338 | 3.959 | 7.297 |
| Triphenylguanidine..... | 1.25 | 5 | Strong, but indistinguishable. Phenyl mus- tard oil could be detected | 7.523 | 4.063 | 3.460 | 3.872 | 7.332 |

the preceding equations. The results obtained for the acetone extracts of the different mixtures, together with all the sulfur estimations made, are also recorded in detail in Table IV. To facilitate comparison, the combined sulfurs, expressed as sulfur coefficients, are tabulated in Table V in the order of their relative magnitude.

TABLE V
First Latex Pale Crêpe..... 92.5 parts
Sulfur..... 7.5 parts
Accelerator..... X parts
Vulcanized for 90 min. at 148° C.

| ACCELERATOR | Com- bined Sulfur Per cent | Sulfur Coef- ficient | Excess (+) Sulfur Coef- ficient |
|-------------------------------------|-------------------------------------|----------------------------|--|
| Phenyl Mustard Oil..... | 1.726 | 1.877 | —0.060 |
| Control (No Accelerator)..... | 1.792 | 1.937 | .. |
| Diphenylthiourea..... | 3.078 | 3.361 | 1.424 |
| Phenyl Mustard Oil and Aniline..... | 3.100 | 3.385 | 1.448 |
| Aniline..... | 3.625 | 3.935 | 1.998 |
| Triphenylguanidine..... | 3.872 | 4.240 | 2.303 |
| Diphenylthiourea and Aniline..... | 3.959 | 4.340 | 2.403 |

From Table V it is seen that the sulfur coefficients obtained confirmed very closely the estimates made upon the physical properties. Further, it is shown that the activity of diphenylthiourea is almost exactly equal to that obtained with an amount of aniline corresponding to the quantity formed in its decomposition products as expressed in Equation 1. Likewise, triphenylguanidine was found to have the same activity as obtained with an equivalent amount of diphenylthiourea and aniline, as required by Equation 2, when the reaction proceeds toward the left.

It is evident that the action of both diphenylthiourea and triphenylguanidine as accelerators is due to their tendency to decompose, under vulcanizing conditions and temperatures, with aniline as one of the most probable degradation products. Moreover, it would appear that the aniline so formed is responsible for the acceleration effected, and owes its activity to the presence of an active group containing nitrogen, which functions as a sulfur carrier. That in no case were we able to recover the original amount of accelerator in the acetone extract, is an indication—and an indication only—that a portion of the active principle may also remain bound to the rubber as well as the sulfur.

Final emphasis is laid upon the fact that all of our results have been obtained with a mixture composed of rubber, sulfur, and accelerator only. The presence in the mixture of inorganic oxides has been found to have a marked influence on both the chemical and physical results obtained after vulcanization.

CONCLUSIONS

In view of the preceding results, we have been led to the following conclusions:

1—Comparisons of organic substances as accelerators should be made with molecularly equivalent amounts of the substances in question, and should be based on the values obtained for their excess sulfur coefficients over that of a control which contains no accelerator.

2—The action of certain substances, such as diphenylthiourea, is due to their tendency to decompose under vulcanizing conditions and temperatures into simpler substances which contain an active nitrogen group which is responsible for the acceleration effected.

3—Molecularly equivalent quantities of substances which contain the same active nitrogen group in their primary nucleus effect the same accelerating activity.

4—The replacement of the hydrogen in the active nitrogen group by other and larger groups, or radicals, decreases the activity of the parent substance.

5—The activity of the nitrogen in certain groups is most readily interpreted as due to a change in valency from three to five, with the temporary addition of sulfur; the active nitrogen group would thus function as a sulfur carrier.

CARBON BLACK—ITS PROPERTIES AND USES^{1,2}

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An investigation of the carbon black industry has been undertaken by the United States Bureau of Mines as a result of economic issues brought up during the war. In the present process of manufacture carbon black is made by burning natural gas with a supply of air insufficient for complete combustion and collecting the liberated carbon on a metal surface by actual contact of the flame on the surface. This process produces from 0.5 lb. to 1.5 lbs. of carbon black from 1000 cu. ft. of gas or 1.5 per cent to 3.5 per cent of the total carbon in the gas. The process at first sight seems most wasteful but examination of the problem shows that it is at any rate the only process in practical operation which produces carbon black

¹ Published by permission of the Director, U. S. Bureau of Mines.

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