THE MECHANISM OF DIPHENYLGUANIDINE AS AN ACCELERATOR
OF VULCANIZATION

DISSERTATION

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Approved by:

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HISTORY OF VULCANIZATION

The process of vulcanization of rubber was discovered within the last century although the crude natural product has been known at least four hundred years. The Spaniard, N. Tillier, in writings about the year 1525 describes explorations in South America where the Indians used balls of crude rubber in a game. Later in 1731, a French geographical expedition into South America brought back descriptions of crude rubber articles used by the natives. The material, crude rubber, was for a long time valueless from a commercial standpoint since it became soft and sticky in summer and hard and non-pliable in winter. Hayward, one of the early investigators who attempted to modify the nature of the product, dusted sulfur on the surface of rubberized fabric and exposed it to the action of the sunlight. Charles Goodyear became interested in this problem and purchased Hayward's patent. In his final series of experiments in 1839 he found that time and temperature were the two factors the control of which effected vulcanization, the term applied to the reaction between rubber and sulfur. Goodyear used in his rubber mixtures the first accelerator of vulcanization,
white lead, as subsequently described in his patent.

The vulcanization process not only eliminated the undesirable properties of the raw rubber due to changing temperature conditions but gave a product of superior tensile strength.

Parkes, in 1846, discovered the process of cold cure vulcanization by the use of sulfur chloride which is now used extensively on small rubber articles and rubberized fabrics.

Hancock, in England, in 1844 claims to have independently discovered vulcanization, however, Goodyear is generally accredited with the discovery.
DISCOVERY AND USE OF ACCELERATORS

By an accelerator of vulcanization is meant any substance, either organic or inorganic, which, when added to the rubber-sulfur mixture, not only hastens the time of vulcanization but also causes a decided change in the physical properties.

The discovery of inorganic accelerators occurred simultaneously with that of vulcanization and white lead, previously mentioned, was the first compound so used. The class of inorganic accelerators includes lead compounds and the oxides of zinc, magnesium and calcium. The hydroxides, hydrosulfides, and sulfides of the alkali metals have also been used to a limited extent.

Organic accelerators, however, are of comparatively recent origin, and their use dates back not more than seventeen years.

The first record, according to Geer\(^\#\), of an organic

\(^\#\) J. Ind. & Eng. Chem. 14, (1922), 369

compound being used as an accelerator of vulcanization was made in 1906. In this year, Censlager, of the Diamond Rubber Company, first used aniline in compounding a rubber mixture and, in February, 1907, the same company made use of thiocarbanilide in a similar way. The experiments so carried out by the Diamond Rubber Company antedate by six years any literature or
patent references on the use of organic compounds as accelerators of vulcanization.

Baeyer and Company, about 1912, discovered that certain strong organic bases were excellent accelerators. Accordingly, they attempted to restrict the use of all nitrogenous substances by a patent which is claimed to cover all bases with a dissociation constant greater than $1 \times 10^{-8}$. This was the first basic patent on organic compounds for use as accelerators of vulcanization in the rubber industry. Previous to the Baeyer patents, a patent had been granted to Wi. and Walther Ostwald for treatment of rubber, gutta-percha with pyridine, quinoline, dimethylaniline, etc. in order to prevent its becoming hard and fragile. The Ostwalds failed, however, to note the accelerating action which certain salts of these compounds possess.

Shortly following the patents for the use of piperidine and its derivatives, Bastide in France patented the use of methylene aniline and related compounds. Later there appeared a variety of specifications covering the use of dimethylamine, D.R.P. 269,512; French Pat. 464,533 aldehyde ammonia, tetra- and hexamethylenediamines, p-phenylene diamine, and naphthylenediamines; the guanidines, D.R.P. 280,198 (1914); U.S.Pat. 1,149,560 (1915) Brit. Pat. 17,760 (1916).
naphthylamine\#; and a larger number of other amino compounds, or
# U. S. Pat. 1,296,469 (1919)
nitrogenous substances, all of which have been previously men-
tioned by King, Peachey, Twiss, Spence, or Ditmar. In their
patents, Baeyer and Company cover the use of the urea and
thiourea derivatives of saturated aliphatic amines with both open
and closed carbon chains. In this connection, it is interesting
to note that in America attention was directed to the use of
urea as an accelerator before the appearance of any patents upon
urea or the thioureas. This was the result of observations upon
certain African rubbers that Vulcanized with more than average
rapidity and which were found to have been coagulated by human
urine. 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.

Bedford\#, ### and Peachy###\# have been granted patents
# U. S. Pat. 1,372,662, -5, -4 (1921)
### Brit. Pat. 139,857 (1919)
###/### Brit. Pat. 113,570 (1917)
on the sulfur reaction product of certain well known accelerators.
For instance, it was shown that if accelerators such as thio-
carbonilid and p-nitroso dimethylaniline be heated first with sul-
fur, that the resulting compounds of unknown composition had a
greater accelerating value than the original accelerators. The
chemistry of these sulfur reaction products have been largely
extended by Bedford, Scott, Bruni, and Boord and Sebrell. Boord
and Sebrell# as well as Bruni and Romani## have isolated from

# Dissertation, Ohio State University, 1922.
## India-Rubber J., 62, (1921) 63; Giorn. chim. ind applicata. 3 (1921) 196

the thiocarbanilid-sulfur reaction mixture the compound

1-mercapto benzothiazol which is a more powerful accelerator than thiocarbanilid.

The accelerators recently developed include metallic salts of alkyl dithiocarbamic acids together with their oxidation products, the thiurams, the xanthates; the metallic salts and oxidation products of dithio acids; and the di substituted guanidines. The di substituted guanidines have proven to be very excellent accelerators. A study of the properties of diphenyl guanidine, and of the mechanism of the acceleration produced by the use of this compound in the process of vulcanization is the purpose of this paper.
THEORIES OF ACCELERATION BY ORGANIC COMPOUNDS

The mechanism of acceleration has received serious consideration only during the last seven years. Within this time, at least seven papers concerned with this basic question have been published and may well be summarized.

A Dubosc developed a hypothesis in which the vulcanizing agent is said to be thiocyanic acid; formed, he believed, by the action of sulfur on the organic accelerator. In this theory, it is assumed that the sulfur is given up again in a more active form to the rubber. The theory is untenable, first, because non-nitrogenous substances are accelerators, second, since derivatives of the mustard oils exert a large influence in many instances and finally, because the theory is not in agreement with the accepted principles of chemistry.

The hypothesis more frequently advanced, and which at present is accepted in one form or another, is that the accelerator combines with the sulfur to be added during vulcanization, to form sulfides or polysulfides, and that the latter compounds are capable of giving up sulfur to the rubber. The accelerator then combines with more sulfur and the process is repeated.

This theory has been proposed in different forms by Ostrominslenaki, by Kratz, Flower and Coolidge, and by

### # J. Ind. and Eng. Chem., 12 (1920), 317.
Ostrominslenski assumed that the amines react with sulfur according to the equation:

\[ 2RNH_2 + 4S \rightarrow RNHS-S-SNRH + H_2S \]

forming trisulfides, so-called thiazonides. This assumption is purely hypothetical, as compounds of this nature have never been isolated.

Kratz, Flower and Coolidge ascribe the action of the amines to the formation of a compound of the formula \( \text{R-NH}_2 \text{S} \) which should be capable of giving up its sulfur and combining with more sulfur alternatively. The only analogous compounds known are the oxides of the dialkyl anilines. Similar derivatives of the secondary bases have never been described.

Scott and Bedford, in their theory, assume that the amines give polysulfides of substituted ammonium derivatives of the type \( \text{R-NH}_2 \text{SH} \) which alternatively combine with sulfur and yield it to the rubber.

These writers classified accelerators as follows:

"1. Organic bases and compounds that form bases under the conditions of vulcanization are believed to form polysulfides thru the aid of hydrogen sulfide."

"2. Thioureas, dithiocarbamates, thiurams, and mercaptan compounds are believed to form polysulfides directly or by
first forming disulfides, and are termed 'carbo sulfhydryl accelerators.'"

Bedford and Sebrell furnished further experimental evidence for the existence of metallic salts of accelerators of class 2. This classification is supported by the two papers of Kratz, Flower and Shapiro concerned with the action of zinc oxide when used in the presence of organic accelerators. These writers assumed the formation of metallic salts to account for the increased activity observed.

Bruni and Romani reported the preparation of \( \text{mercapto benzothiazol} \) by the action of sulfur on thiocarbanilid, and upon the formation of its disulfide and its reactions advanced a theory to account for the mechanism of the action of thiourea and dithiocarbamate accelerators.

The classification of accelerators as proposed by these writers is important and divides them into three types as follows:

"1. Basic substances, inorganic and organic."

"2. Aromatic nitroso derivatives."

"3. Sulfurated substances derived from thiourea or containing the groups \(-C=S-\) or \(-C\overset{S}{\underset{S}{\text{S}}}\)."
Bedford and Sebrell\# in a recent paper, pointed out
where the theory advanced by Bruni and Romani is somewhat in
error and proposed a modified theory, thus:

"Organic accelerators in absence of secondary
accelerators function as follows:

\[ \text{R-H} + \text{S} \rightarrow \text{R-SH} \]
\[ 2\text{RSH} + \text{S} \rightarrow \text{R-S-S-R} + \text{H}_2\text{S} \]
\[ \text{R-S-S-R} + \text{S}_{\text{x}-2} \rightarrow \text{R-S}_{\text{x}}\text{-R} \]
\[ \text{R-S}_{\text{x}}\text{-R} \rightarrow \text{R-S-S-R} + \text{S}_{\text{x}-2} \cdot \text{active sulfur} \]

"Allowing R to represent either hydrogen, metal, or radical, the
entire mechanism of vulcanization with accelerators may be
summed up in one equation:

\[ \text{R-S}_{\text{x}}\text{-R} \rightarrow \text{R-S-R} + \text{active sulfur} "\]

In concluding this summary of the theories of acceleration, it should be pointed out that at present we have no
definitely established theory of acceleration and that every
new publication of experimental evidence is being accompanied
by a new theory.
DIPHENYLGUANIDINE AS AN ACCELERATOR.

The accelerating properties of diphenylguanidine were probably first observed by Kratz in 1916-17. Certainly Kratz, Flower and Coolidge were the first to publish an account of the disubstituted guanidines as accelerators of vulcanization. These investigators pointed out the higher curing power of mono- and diphenyl guanidine as compared with the triphenyl derivative, showing the mono- and diphenyl derivatives to be about six times more active as accelerators than triphenyl guanidine, when considered part for part.

King recommended the use of certain derivatives of urea such as guanidine and Twiss in 1917 worked with amino guanidine bicarbonate.

Apparently, Weiss was the first to overcome the technical difficulties involved in the use of diphenylguanidine as an accelerator and, in 1922 a patent was granted him covering this use.

Recently Brumbaugh has given a detailed account of a synthesis of diphenyl guanidine which is a modification
of the method described by Weiss in his patent#

# U. S. Patent 1,422,506

Bedford and Sebrell## and Scott### have published

## J. Ind. & Eng. Chem. 14 (1922) 30
### J. Ind. & Eng. Chem. 15 (1923) 286

more on the reactions involved in the use of diphenyl
guanidine as an accelerator than any of the other investigators.

From the work done up to the present time it seems
that the cause of the accelerating action of diphenylguanidine
is to be sought in either of two directions:

First: - Diphenylguanidine readily undergoes decomposition
and the decomposition products either directly or in combina-
tion with sulfur may be responsible for the accelerating
action.

Second: - Diphenylguanidine may form reaction products with
sulfur or sulfur compounds, known to be present in the compound-
ed rubber mixture under the conditions of vulcanization, the
sulfur derivatives thus produced acting as the accelerating
agents.

In discussing the first hypothesis Scott### mentions

#### J. Ind. & Eng. Chem. 15 (1923) 286

as decomposition products of diphenylguanidine, ammonia, aniline,
and triphenyl dicarbimid, an observation first made by Rathke
and Oppenheim##### and points out that although ammonia is a

##### Ber. 12 (1879) 774; 23 (1890) 1669

powerful accelerator, the other compounds are relatively weak
in this respect. He concludes then that this decomposition is not primarily involved in the accelerating reaction.
Scott, however, failed to account for the formation of the triphenyl dicarbimid and overlooked the very evident possibility of diphenylguanidine undergoing a primary decomposition.

Largely from this negative evidence, Scott inclines to the second hypothesis. He concludes that diphenylguanidine is a hydrosulfide accelerator, a classification previously used by Bedford and Sebrell under the term of "hydrogen sulfide-polysulfide accelerator."

The heat decomposition products of diphenylguanidine as carried out under pressure are ultimately:

1. Ammonia, $\text{NH}_3$
2. Aniline, $\text{C}_6\text{H}_5\text{NH}_2$
3. Tetraphenylmelamine

$$
\text{C}_6\text{H}_5\text{N} = \text{C} \quad \text{NH} \quad \text{C} = \text{NC}_6\text{H}_5
$$

4. Triphenyl dicarbimid

$$
\text{C}_6\text{H}_5\text{N} = \text{C} \quad \text{NH} \quad \text{C} = \text{NC}_6\text{H}_5
$$

Rathke and Oppenheim# first observed that diphenylguanidine decomposes at temperatures above its melting point with the formation of ammonia, aniline, and triphenyl dicarbimid. It should be pointed out that when this decomposition occurs under pressure as in vulcanization that the yield of tetraphenyl

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# Ber. 12 (1879) 774; 23 (1890) 1669
melamine is increased at the expense of the triphenyl dicarbimid.

Rathke\footnote{Ber \textbf{20} (1887) 1065} interpreted the formation of triphenyl dicarbimid and tetraphenyl melamine by assuming that the primary decomposition of diphenylguanidine takes place in two ways as follows:

1. \[ \text{C} = \text{NH} \ \ \ \text{NHC}_6\text{H}_5 \ \ \rightarrow \ \ NH_3 \ \cdot \ \text{C(NC}_6\text{H}_5)_2 \ \text{diphenyl carbimid} \]

2. \[ \text{C} = \text{NH} \ \ \ \ \text{NHC}_6\text{H}_5 \ \ \rightarrow \ \text{C}_6\text{H}_5\text{NH}_2 \ \cdot \ \text{C}_6\text{H}_5\text{NHCN} \ \text{phenyl cyanamid} \]

Then under the temperature at which the reaction is carried out, tetraphenyl melamine and triphenyl dicarbimid are formed by the interaction of diphenyl carbimid and phenyl cyanamid in the correct proportions. Expressed in the form of equations:

3. \[ 2\text{C}_6\text{H}_5\text{NHCN} + \text{C(NC}_6\text{H}_5)_2 \rightarrow \text{C}_6\text{H}_5\text{N} = \text{C} \ \text{C(NC}_6\text{H}_5)_2 \]

4. \[ \text{C}_6\text{H}_5\text{NHCN} + \text{C(NC}_6\text{H}_5)_2 \rightarrow \text{C}_6\text{H}_5\text{N} = \text{C} \ \text{C(NC}_6\text{H}_5)_2 \]

Since it is known that mono- and diphenylguanidine have nearly the same value as accelerators, it is logical to assume that these two compounds have some property or properties in common which is responsible for the accelerating action. On the other hand, triphenylguanidine is a relatively slow accelerator and therefore must lack the property peculiar to the
mono- and diphenyl derivatives. Comparing the heat decomposition products of the three derivatives we find

**Monophenylguanidine**

\[
\text{NH}_3 + \text{C}_6\text{H}_5\text{NHCN}
\]

**Diphenylguanidine**

\[
\text{NH}_3 + \text{C}
\]

**Triphenylguanidine**

\[
\text{NH}_3 + \text{C}_6\text{H}_5\text{NHCN}
\]

It is evident that the decomposition products ammonia and phenyl cyanamid occur in the decomposition of both mono- and diphenylguanidine. Further, aniline and diphenyl carbimid occur in the decomposition of triphenylguanidine but are not found in the case of monophenylguanidine. The conclusion drawn is that the ammonia and phenyl cyanamid, acting separately or together, may be responsible for the rapid accelerating value of mono- and diphenylguanidine.
The work done by Sebrell on the isolation of 1-mercaptobenzothiazol, as previously mentioned, from the thiocarbanilid-sulfur reaction mixture suggests the possibility that diphenylguanidine may form similar derivatives when heated with sulfur under pressure to which the accelerating action may be attributed.

Ammonia has proven to be a powerful accelerator and its power as an accelerator is ascribed to the fact that it readily forms hydrosulfides, sulfides and polysulfides. Analogously, the basic amino group of diphenylguanidine should also form hydrosulfide, sulfide, and polysulfide derivatives which should accelerate the process of vulcanization to the same or greater degree than free diphenylguanidine.
THE AIM AND SCOPE OF THE PRESENT WORK.

It is evident that the sum total of experimental results accumulated in previous investigations is not sufficiently exhaustive to permit any final and logical conclusion to be drawn. The purpose of the present work has been, therefore, to study carefully the accelerating action of diphenylguanidine with both views in mind. The investigation has proceeded naturally through the following phases:

1. A study of the decomposition products of diphenylguanidine and a measurement of their accelerating values both singly and collectively as well as those of their sulfur reaction products.

2. An examination of the fusion mixture of diphenylguanidine with sulfur when heated under pressure, for the purpose of determining whether derivatives analogous to the mercapto benzothiazoles are formed to which the accelerating action can be attributed.

3. An extension of our knowledge of the chemistry of diphenylguanidine particularly as regards the several possible sulfur derivatives and measurement of their accelerating values.

4. A careful study of the reaction of diphenylguanidine with hydrogen sulfide as well as sulfur in an attempt to separate a hydrosulfide, sulfide, or polysulfide having as high an accelerating action as the free diphenylguanidine when used in equivalent quantities.
5. It has also been found advisable to measure the accelerating values of a number of miscellaneous sulfur derivatives for the purpose of testing the validity of the conclusion reached independently by Sebrell and Boord as well as by Bruni and Romani that the peculiar accelerating power attaches to the \(-\text{C-SH}\) grouping.
EXPERIMENTAL PART

HEAT DECOMPOSITION PRODUCTS OF DIPHENYLGUANIDINE.

Tetraphenyl melamine, \( \text{C}_6\text{H}_5\text{N} = \text{C} \rightarrow \text{NH} \)

One mole (211 grams) of diphenylguanidine was heated in an autoclave for four hours. The temperature rose to 200\(^\circ\) C during a period of two hours; the current was then shut off and after cooling to 150\(^\circ\) C, the autoclave was taken from the furnace and the contents removed. The odors of ammonia and aniline were strongly evident and the reaction mixture upon cooling partially solidified to a mass weighing 170 g.

The reaction mixture was digested with 350 cc. of boiling alcohol and then allowed to stand four hours in the ice box. A precipitate deposited which was filtered off, dissolved in a large volume of alcohol and treated with boneblack. A small insoluble residue was filtered off and the solution allowed to stand over night whereupon fine white needle-like crystals deposited. The crystals were filtered off, washed with dilute alcohol and dried in the air. The yield was forty grams of tetraphenyl melamine, melting at 222\(^\circ\) C.

The filtrate from the above solution on being poured into water yielded a white curdy precipitate, which, after drying, weighed 28 grams and melted at 220\(^\circ\) C.

The total yield of tetraphenyl melamine obtained was 68 grams or 40% as calculated on the basis of diphenylguanidine used.
Triphenyldicarbimid. \[ \text{C}_6\text{H}_5\text{N} \rightleftharpoons \text{C}_6\text{H}_5\text{N} \]

The filtrate from the original digestion mixture was heated to boiling and acidified with concentrated hydrochloric acid. A heavy precipitate formed which was filtered off. This precipitate, consisting of the hydrochloride of triphenyldicarbimid was digested with alcohol and made strongly alkaline by the addition of solid sodium carbonate. The alcoholic solution was then poured slowly into water with stirring and the white flocculent precipitate formed extracted with ether. After evaporation of the ether, the residue was taken up in alcohol and the solution treated with boneblack. On standing over night, long needles slightly yellow in color were deposited. The free base, triphenyldicarbimid, contained alcohol of crystallization and melted 70-72° C. The yield was thirty grams.

Diphenyl carbimid. \[ \text{C}_6\text{H}_5\text{N} \]

Three methods previously described in the literature were tried out in the preparation of this compound.

1. The method proposed by Herzog\(^\#\) in which thiocarbamid  
\(^\#\) Zeit. Angew Chem. 33 I (1920) 140  
is desulfurized by the use of arsenic trioxide.

Thiocarbanilid, 150 grams, was suspended in 600 cc. toluene and 87 grams of arsenic trioxide added. The reaction mixture digested at the boiling point for five hours and
filtered hot to remove the red and yellow arsenic sulfides. The toluene was then removed by distillation under diminished pressure and the residue fractionated below 20 mm. pressure. The major portion came over below 200° C, but a small fraction was collected from 200 - 220° C. The product appeared to be a mixture of unchanged thiocarbanilid and diphenyl carbimid.

2. The method proposed by Weith in which triphenylguanidine is decomposed by heat.

# Ber. 7, 1306 (1874)

Triphenylguanidine, 200 grams, was distilled under ordinary pressure. The fraction distilling between 300-350° C. was collected separately and weighed 70 grams. This fraction was redistilled under 30 mm. pressure and then once more at atmospheric pressure. The portion collected between 300-320° C. weighed 10 grams and appeared to be almost pure diphenyl carbimid.

3. Another method described by Weith consists in desulfurizing thiocarbanilide by heating with mercuric oxide.

# Ber. 7, 10 (1874)

Thiocarbanilid, 125 grams, was suspended in 250 cc. of boiling benzene and 220 grams of yellow mercuric oxide added portionwise over the course of half an hour with vigorous stirring. The solution gave a negative test with ammoniacal silver nitrate indicating complete desulfurization of the
thiocarbanilid. The mercuric sulfide was filtered from the hot solution and the benzene immediately distilled off. The residue was then fractionated under ordinary pressure with the following results.

1. Fraction 290-305° C., 18 grams - Brittle resin
2. Fraction 305-320° C., 21 grams - Semi-solid.

These two portions were re fractionated under diminished pressure yielding a distillate boiling at 215-220 under 31 mm. and weighing 27 grams.

This product was tested by dissolving in benzene and passing in hydrogen sulfide whereby thiocarbanilid melting at 152° was regenerated. It was found in using the above method that yellow mercuric oxide was far more satisfactory in desulfurizing the thiocarbanilid than the red modification. Of the three procedures the latter proved to be the most satisfactory.

Phenyl cyanamid, C₆H₅NHCN, was prepared by the method described by Hofmann#.

# Ber. 19 (1885) 3217

Monophenylthiourea, 115 grams, was dissolved in two liters of a ten per cent solution of sodium hydroxide by heating to 80° C. and 500 grams of lead acetate added portionwise. The reaction mixture was heated on the water bath for fifteen minutes and the lead sulfide filtered off. After the filtrate had cooled to room temperature, a slight excess of acetic acid
was added whereupon phenyl cyanamid precipitated as a white crystal meal. After standing an hour, the deposit was filtered off and dried. Yield 72 grams of phenylcyanamid or 75% of the theoretical calculated on the basis of the monophenyl thiourea used.

The phenyl cyanamid after recrystallization from water melted at 45-47° C.

**Phenyl cyanamid - Sulfur Reaction.**

Phenylcyanamid, 65 grams, and sulfur 10 grams were heated in a bomb tube for four hours at a temperature of 150-160° C. Upon opening the tube a considerable pressure was released, and a strong odor of hydrogen sulfide observed. The contents of the tube showed evidence of carbonization. The product was removed by warming with about 100 cc. benzene giving a thick black mixture. Thirty grams of original reaction product were digested with 200 cc. of alcohol and filtered, leaving 3 grams of an insoluble residue. From the filtrate, by dilution with water and the addition of a trace of sodium hydroxide, a cream colored precipitate was deposited, which after drying weighed 10 grams. This substance was redissolved in 100 cc. alcohol filtered and the solution diluted with 30 cc. water. The resulting solution was treated with boneblack and filtered. The filtrate was brought to boiling and allowed to cool slowly. Only a small non-crystalline precipitate was deposited.
Diphenyl carbimid - Sulfur Reaction.

Diphenyl carbimid, 35 grams, and sulfur, 4 grams, were heated in a bomb tube for four hours at a temperature of 150-160° C. Upon opening the tube, only a slight pressure was evident, the reaction mixture showing a slight odor of carbamidine. The product which appeared to be partially crystalline, was removed from the tube by warming gently with about 50 cc. benzene. After the mixture had cooled, the insoluble residue was filtered off and when dry weighed 22 grams. This residue was crystallized from carbon disulfide and yielded 10 grams of fine white needles melting 157-8° C. The compound contained carbon, hydrogen, and nitrogen and proved to be a crystalline form of diphenyl carbimid.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>79.34%</td>
<td>80.35%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80.31%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.43%</td>
<td>5.66%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.71%</td>
</tr>
</tbody>
</table>

Diphenylguanidine - Sulfur Reaction.

Diphenylguanidine, 225 grams, and sulfur, 25 grams, were heated in the autoclave to a maximum temperature of 220° during the course of two hours when the current was shut off and the autoclave allowed to cool down in the furnace. On opening the autoclave there was only a slight pressure but the contents smelled strongly of hydrogen sulfide, ammonia and aniline. The reaction mixture weighed 150 grams, and was quite liquid when warm but on standing in the air gradually
became a semi-solid, sticky mass.

A portion of the reaction mixture, 100 grams, was digested with 200 cc. of boiling alcohol and the mixture allowed to stand four hours in the ice box. The insoluble grayish green residue when filtered off and dried weighed 35 grams. It was redissolved in 1200 cc. of hot alcohol, treated with boneblack, filtered and allowed to stand over night. Slightly yellow needle-like crystals deposited which were filtered off, washed with dilute alcohol and dried. These crystals proved to be tetraphenylmelamine, weighed 19 grams and melted at 220-220°C.

The filtrate from the original alcoholic mother liquor was heated to boiling and acidified with hydrochloric acid. On standing four hours, a precipitate deposited which was filtered off, dissolved in 150 cc. alcohol and treated with sodium carbonate until alkaline. The solution was poured into water, the flocculent precipitate filtered off and dissolved in alcohol. The solution was treated with boneblack, allowed to stand over night. The needle crystals which deposited were filtered off and dried. The product weighed 8 grams, melted at 220°C and proved to be tetraphenylmelamine.

With the exception of tetraphenylmelamine and aniline, no other pure compound was isolated from the reaction mixture.
SUBSTITUTED DITHIOCARBAMATES

Diphenylguanidine phenyldithiocarbonate, \( \text{C}_7\text{H}_5\text{N}_2\text{S}_2 \)

Diphenylguanidine, 100 grams, was dissolved in one liter of alcohol by heating and 50 grams of aniline added. The solution was filtered, cooled to room temperature and 45 grams of carbon disulfide added with stirring. The reaction mixture was placed in a dish of crushed ice and allowed to stand over night. The slightly yellow diamond shaped plates which deposited were filtered off, washed twice with ether and dried. Yield 150 grams of diphenylguanidine phenyl dithiocarbonate melting 125.5\(^o\)C. The analysis was as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>BaSO(_4)</th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>.2460</td>
<td>.3036</td>
<td>16.84</td>
<td>16.95</td>
</tr>
</tbody>
</table>

This compound is quite insoluble in the cold in the common organic solvents and on heating in the presence of the solvent is decomposed, regenerating diphenylguanidine. Various solvents were used in carrying out the above reaction but ethyl alcohol was found to give the best results.

Scott\(^\#\) observed that this compound on refluxing in benzene decomposed to give chiefly as the final product, triphenylguanylthiourea. This observation was confirmed by our work as follows:

\(^\#\) J. Ind. & Eng. Chem. 15 (1923) 286
Triphenylguanylthiourea.

Diphenylguanidine phenylidithiocarbamate, 100 grams, was suspended in one liter of benzene and the mixture refluxed for fifteen hours. At the end of two hours, it was noted that all material was in solution. After fifteen hours of refluxing, a small oily layer had separated in the bottom of the flask. The benzene layer was decanted from this oily layer and on standing over night deposited coarse needle-like crystals. These crystals were filtered off, washed twice with alcohol, yielding 28 grams of triphenylguanylthiourea. This product on recrystallization from benzene, melted at 160° C. as compared to 157° C. reported by Scott. #

# J. Ind. & Eng. Chem. 15 (1923) 286

It was found that diphenylguanidine phenylidithiocarbamate could also be prepared by the interaction of diphenylguanidine on ammonium phenylidithiocarbamate.

Ammonium phenylidithiocarbamate, 9.25 grams, was dissolved in a little water and 150 cc. of alcohol added. A solution of diphenylguanidine, 10.5 grams, in 150 cc. ethyl alcohol was poured into the solution of the ammonium salt with vigorous stirring. A heavy crystalline precipitate deposited after about two minutes. After the mixture had stood for two hours, this precipitate was filtered off, washed with water and ether and dried. This product was identified as diphenylguanidine phenylidithiocarbamate by its melting point 122-4° C. The yield was 18 grams or 94%.
Diphenylguanidine salts of the Aryldithiocarbamic Acid.

The diphenylguanidine salts of a number of derivatives of phenyldithiocarbamic acid were prepared by the following general method. The general reaction involved is:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{N} & \text{NHCNH}_2 + \text{RNH}_2 + \text{CS}_2 \rightarrow \text{R-}NH-C\text{-SH}\cdot\text{NH}_2\cdot\text{C} \text{NC}_6\text{H}_5 \\
\text{C}_6\text{H}_5\text{NH} & \text{NHCNH}_2 \\
\end{align*}
\]

Diphenylguanidine, 25 grams, was dissolved in 250 cc. of alcohol by heating and one equivalent of the arylamine added. The solution was cooled to room temperature and 13 grams (45 percent excess) of carbon disulfide stirred into the mixture. After standing in a cool place for several hours, crystallization of the diphenylguanidine salt began and could be hastened by stirring. When deposition was complete, after about three hours, the product was filtered off, washed with ether and dried. These compounds are very unstable and either the action of heat or the act of solution is sufficient to cause their decomposition. Recrystallization of any of these compounds was therefore impossible.

A summary of the description of these compounds, including the physical characteristics and analyses, is tabulated on the following page.
| Compound | Cmpd | Co. | Title | Yield | Physical char.
|----------|------|-----|-------|-------|------------------
|            |      |    |       |       |                  |
|            |      |    |       |       |                  |
|            |      |    |       |       |                  |
|            |      |    |       |       |                  |
|            |      |    |       |       |                  |

**The Determination of Derivatives of Hydroxyiminodiacetic Acid**
The preparation of the diphenylguanidine salts of substituted phenylidithiocarbamic acids was attempted using the following arylamines:

orthochloraniline
orthoiodoaniline
orthoaminophenol
orthonitroaniline
paranitroaniline
2,4 dichloraniline
3 nitro 4 aminotoluene
anthranilic acid
paraphenylenediamine
aminazoazobenzene

but in every case either no product was obtained or else the substance precipitated as an oil or contaminated with tar.

**Diphenylguanidine phenyldithiocarbizinate.**

Diphenylguanidine, 10 grams, and 4 grams of carbon disulfide were dissolved in 100 cc. alcohol and 20 cc. ether. The cooled solution was added to 5.4 grams of phenylhydrazine in 50 cc. of alcohol and the mixture allowed to stand. After ten minutes, crystals began to form and the reaction mixture was placed in the ice box for four hours. The crystals were then filtered off, washed with ether and dried. The diphenylguanidine phenyl dithiocarbizinate weighed 16 grams and melted at 135.5° C.

In order to confirm the constitution of the above compound, diphenylguanidine was coupled with ammonium phenyl dithiocarbizinate as follows: Ammonium phenyldithiocarbizinate, 10 grams, dissolved in 60% alcohol was added to a solution of 10 grams of diphenylguanidine in 90 cc. of alcohol and 300 cc.
ether. After standing five hours at room temperature a heavy
deposit of crystals had deposited which were filtered off,
washed with ether and dried. The diphenylguanidine phenyl-
dithiocarbizinate weighed 12 grams and melted at 135° C.

This latter experiment confirmed the fact that the
diphenylguanidine salt of phenylthiocarbazinic acid is
formed rather than the phenylhydrazonium salt of diphenyl-
guanyldithiocarbamic acid. The analysis was as follows:

<table>
<thead>
<tr>
<th>Subst.</th>
<th>BaSO₄</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.2110 gms</td>
<td>.2407 gms</td>
</tr>
</tbody>
</table>

Diphenylguanidine Salt of l-mercaptobenzothiazole,
\[
\text{C-SH} \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_5 \text{NHC}_6\text{H}_5
\]

Since l-mercaptobenzothiazole contains the group
\(-\text{S} \cdot \text{C-SH}\) which has similar properties to the group in dithio-
carbamic acid \(-\text{N} \cdot \text{C-SH}\) it was believed that diphenylguanidine
would form a salt in the same way as the substituted di-
thiocarbamic acids.

Diphenylguanidine, 20 grams, was dissolved in 200 cc.
alcohol by heating. To this solution, 15 grams of l-mercapto-
benzothiazole dissolved in 125 cc. alcohol was added and the
mixture heated to boiling point. After the reaction mixture
had stood at room temperature for 36 hours, yellow needles be-
gen to deposit. The crystal mass was filtered off, washed with
alcohol and dried. The product proved to be diphenyl-
guanidine 1-mercaptobenzothiazole, weighed 10.5 grams and
melted at 167-8° C. The analysis was as follows:

<table>
<thead>
<tr>
<th>Subst.</th>
<th>BaSO₄</th>
<th>Sulfur Calculated</th>
<th>Sulfur Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>.2061</td>
<td>.2604</td>
<td>16.93%</td>
<td>17.36%</td>
</tr>
</tbody>
</table>
REACTION PRODUCT BETWEEN DIPHENYLGUANIDINE AND CARBON DISULFIDE

The purpose in view in carrying out this experiment was to attempt the preparation of diphenylguanylthiourea. It was thought that the reaction might proceed through the following stages:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{N} & \xleftarrow{} \text{CNH}_2 + \text{CS}_2 \quad \rightarrow \quad \text{C}_6\text{H}_5\text{N} \xleftarrow{} \text{CNHCSH} \\
\text{C}_6\text{H}_5\text{NH} & \xleftarrow{} \text{CNHCSH} \quad \rightarrow \quad \text{C}_6\text{H}_5\text{NH} \xleftarrow{} \text{CNHCSH} \cdot \text{H} \cdot \text{NH}_2 \cdot \text{NHC}_6\text{H}_5 \\
\text{C}_6\text{H}_5\text{N} & \xleftarrow{} \text{CNHCSH} \cdot \text{NH}_2 \cdot \text{C} \quad \xrightarrow{\text{oxidize}} \quad \text{C}_6\text{H}_5\text{NH} \xleftarrow{} \text{C-NH} - \text{C-NH} - \text{C} \cdot \text{NHC}_6\text{H}_5 \\
\text{C}_6\text{H}_5\text{NH} & \xleftarrow{} \text{CNHCSH} \cdot \text{NH}_2 \cdot \text{C} \quad \xrightarrow{-\text{H}_2\text{S}} \quad \text{C}_6\text{H}_5\text{NH} \xleftarrow{} \text{C-NH} - \text{C-NH} - \text{C} \cdot \text{NHC}_6\text{H}_5
\end{align*}
\]

Hydrogen peroxide was used to oxidize, if possible, the hydrogen sulfide and carry the reaction through to the formation of the substituted thiourea, diphenylguanylthiourea.

Recrystallized diphenylguanidine, 20 grams, was dissolved in 150 cc. of cold alcohol and 4 grams of carbon disulfide added. The solution was cooled to \(-10^\circ\) C. and 7 grams of 30% hydrogen peroxide slowly stirred in. The reaction proceeded quite rapidly and considerable heat was developed. After the mixture had been stirred for fifteen minutes, it was allowed to stand in the ice box over night after which a few large crystals had formed. The mixture was stirred thoroughly for four hours whereupon a considerable deposit of crystal meal
was thrown down. This precipitate was filtered off, washed twice with ether and dried. The compound weighed 16 grams and melted at 151° C.

The analysis was as follows:

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>6.89%</td>
<td>4.39%</td>
</tr>
</tbody>
</table>

Since the sulfur content as found does not agree with the theoretical as calculated for \( \text{N}_{4}\text{H}(\text{diphenylguanyl})\text{thiourea}, \) the composition of this compound is not known.
DIPHENYL GUANIDINE SULFIDE

Diphenylguanidine, 40 grams, was suspended in 600 cc. of 95% ethyl alcohol and the mixture cooled below 10\degree C. in an ice bath. Hydrogen sulfide was then passed into the mixture for two hours at the end of which time, a clear lemon yellow solution was obtained. The solution was transferred to a large crystallizing dish and allowed to stand at room temperature for twenty-four hours when diphenylguanidine sulfide crystals began to appear. These sulfide crystals were allowed to grow for two days when needles of diphenyl guanidine began to separate. The sulfide crystals were filtered off, digested with absolute alcohol in the cold to remove all diphenylguanidine and finally air dried. The yield of diphenylguanidine sulfide was 14 grams and the product melted at 134-5\degree. The crystals had the form of irregular cubes.

In the preparation of this compound, the proper concentration of the diphenylguanidine in the solvent and the proper dilution of the alcohol with water determines the conditions most favorable for the formation of this sulfide derivative, free of diphenylguanidine.

Based on the analysis and the properties of the substance, the structure assigned to diphenylguanidine sulfide is:

$$\text{C}_6\text{H}_5\text{N} \rightleftharpoons \text{C-NH}_3$$
$$\text{C}_6\text{H}_5\text{NH} \rightleftharpoons \text{S}$$
$$\text{C}_6\text{H}_5\text{NH} \rightleftharpoons \text{CNH}_3$$
The analysis was as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{BaSO}_4$</th>
<th>Sulfur Calculated</th>
<th>Sulfur Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>.2364</td>
<td>.1130</td>
<td>7.01</td>
<td>6.56</td>
</tr>
<tr>
<td>.2460</td>
<td>.1182</td>
<td>7.01</td>
<td>6.59</td>
</tr>
</tbody>
</table>

On attempting to recrystallize diphenylguanidine sulfide from alcohol, it was found that the resulting product obtained was diphenylguanidine. It is assumed that hydrolysis took place, regenerating the free base.

The following observation was made; which is evidence in favor of a possible intermediate hydrosulfide derivative of diphenylguanidine. When hydrogen sulfide was passed into a cold concentrated alcoholic solution of diphenylguanidine, after about an hour a heavy crystalline precipitate was thrown down. On attempting to filter off this precipitate and dry it under the most carefully controlled conditions, the product always lost hydrogen sulfide and only free diphenylguanidine was obtained as the final product. The following series of equations probably best explain the formation of the intermediate hydrosulfide and the stable sulfide.
1. \[ \text{C}_6\text{H}_5\text{NH}_2 \overset{\text{C-NH}_2 + \text{H}_2\text{S}}{\rightarrow} \text{C}_6\text{H}_5\text{NH} \overset{\text{C-N-H}}{\rightarrow} \text{C}_6\text{H}_5\text{N} \overset{\text{SH}}{\rightarrow} \text{C}_6\text{H}_5\text{N} \overset{\text{SH}}{\rightarrow} \text{C}_6\text{H}_5\text{N} \overset{\text{SH}}{\rightarrow} \text{C}_6\text{H}_5\text{N} \]

2. \[ \text{C}_6\text{H}_5\text{NH} \overset{\text{C-N-H}}{\rightarrow} \overset{\text{H}}{\rightarrow} \overset{\text{HN-C}}{\rightarrow} \overset{\text{NHC}_6\text{H}_5}{\text{NHC}_6\text{H}_5} \]

3. \[ \text{C}_6\text{H}_5\text{NH} \overset{\text{C-NH}_3}{\rightarrow} \overset{\text{H}_3\text{N-C}}{\rightarrow} \overset{\text{NHC}_6\text{H}_5}{\text{NHC}_6\text{H}_5} \overset{\text{H}_2\text{S}}{\rightarrow} \text{H}_2\text{S} \]
MISCELLANEOUS DERIVATIVES

Synthesis of 1-Mercaptobenzothiazole.

The mixture of reagents was introduced into a bomb tube: 10 grams orthiodoaniline, 4 grams carbon disulfide, 2 grams sodium hydroxide and 60 grams absolute alcohol. The tube was sealed and heated at 130° C. for two hours. After cooling and opening tube, the amorphous deposit which had formed was filtered off. This substance proved to be of an inorganic nature and was easily soluble in water. The filtrate was evaporated to dryness, digested with water and a small insoluble residue filtered off. On acidifying the filtrate, a copious precipitate was thrown down. This precipitate was redissolved in dilute sodium carbonate solution and precipitated with dilute hydrochloric acid. The product was filtered off, washed with water and dried. The product proved to be 1-mercaptobenzothiazole and melted at 175° C. as compared to the melting point of 177° C. reported by Sebrell.

The analysis was as follows:

<table>
<thead>
<tr>
<th>Subst.</th>
<th>BaSO₄</th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>.2078 grams</td>
<td>.5802 grams</td>
<td>38.32%</td>
<td>39.29%</td>
</tr>
</tbody>
</table>

The identity of this compound was further confirmed by preparing the disulfide of 1-mercaptobenzothiazole as follows: The 1-mercaptobenzothiazole as obtained above, was dissolved in ammonium hydroxide and oxidized with an alcoholic
solution of iodine. The precipitate was filtered off, extracted with boiling benzene and the insoluble residue filtered off. The filtrate on cooling deposited rosettes of crystals which when recrystallized from alcohol melted at 176-7°C. This agrees well with the melting point of 176°C as reported by Sebrell for the disulfide of 1-mercaptobenzothiazole.
1-Phenyl-2-phenylimido-5-thio-3,4-disulfazolidin. \( \text{C}_6\text{H}_5\text{N}=\text{C} \)

This compound was prepared from ammonium phenyl dithiocarbamate according to the method used by Freund and Bachrach\#.

\# Ann. 285 (1895) 184

Ammonium phenyl dithiocarbamate, 100 grams, was suspended in 500 cc. ligroin and treated dropwise with 155 grams of bromine in 150 cc. of ligroin, the mixture being stirred mechanically. The reaction proceeded with a considerable evolution of heat and hydrogen bromide was liberated in a steady stream. The pulverized salt was colored red and balled together into lumps which were crushed from time to time with a spatula. The stirring was continued for half an hour after all of the bromine had been added. The orange colored product, which fumed in the air, was filtered off and washed thoroughly with ligroin. It was then boiled with 200 cc. of alcohol until solution was complete and allowed to stand over night. The deposit which separated was filtered off and extracted with 200 cc. of benzene. The ammonium bromide residue was filtered off and the benzene filtrate evaporated to dryness. The residue on recrystallization from alcohol formed long yellow needles. The product, 1-phenyl 2-phenylimido-5-thio-3,4-disulfazolidin, weighed 8 grams and melted 154-6\(^\circ\) C. which agrees with the melting point reported by Freund and Bachrach.
Phenyldithiobiazolonethiol. \( \text{C}_6\text{H}_5\text{N}_2\text{S} - \text{C} - \text{S} \text{H} \)
\[
\begin{array}{c}
\text{H} \\
\text{C} - \text{S} - \text{S} \\
\end{array}
\]

This compound was prepared by method described by Busch\#. Phenylhydrazin, 5 grams, dissolved in 20 grams of absolute alcohol, and treated with 12 grams of carbon disulfide. The reaction mixture set to a crystalline mass and then, under warming, 6 grams of potassium hydroxide in 30 grams of absolute alcohol was added. The mixture was refluxed at the boiling point for 20 hours and filtered hot. The filtrate on cooling deposited long fine yellow needles, which were filtered off, washed with ether and dried. The potassium salt of phenyl dithiobiazolonethiol weighed 9 grams and melted 239\( ^\circ \) C.

The potassium salt was dissolved in 200 cc. water, the solution cooled with ice and acidified carefully with dilute hydrochloric acid. The white needle like crystals were filtered off, washed with water and dried at 50\( ^\circ \) C. The free phenyl dithiobiazolonethiol weighed 6 grams and melted at 69\( ^\circ \) C, as compared with the melting point of 90-91\( ^\circ \) C. reported by Busch. This compound is quickly converted into the disulfide on standing and exposure to light.

Thiobiazoldisulfhydrat. \( \text{HS} - \text{N} \cdot \text{N} - \text{OS} \text{H} \) was prepared by the method described by Busch\##. Hydrazin sulfate, 20 grams, was dissolved, by heating, in 250 cc. of water and the solution transferred to a two liter round bottom flask provided with a reflux condenser.
Carbon disulfide, 40 grams, was diluted with 50 cc. of alcohol and added thru the condenser. A solution of 22 grams of potassium hydroxide in 100 cc. of alcohol was introduced in small portions, whereby the liquid boiled vigorously for a time. The reaction mixture was refluxed on the water bath for three hours and the white crystalline mass of potassium sulfate filtered off. The free sulfhydrylate was precipitated in the form of glittering white needles from the filtrate by the addition of 500 cc. of concentrated hydrochloric acid. The product was quickly filtered off and dried by pressing on a porous plate. The yield of crude product was 15 grams. The thiobiazoldisulfhydrylate on recrystallization from ether yielded 13 grams of glittering crystals which melted at 168° C. as compared to 167-8° C. reported by Busch.

\[ \text{\textit{Sulfhydrylbenzimidazol}} \]

This compound was prepared by two methods as described by Kym # and Gucci## respectively. The method of Gucci gave

\[ ^{\#} \text{J. pr. Chem. 75, 323} \]
\[ ^{##} \text{Ga2. 23 (1) 296} \]

the purest product.

The method of Kym was carried out as follows: Ortho phenylenediamine hydrochloride, 27 grams, was fused with 12 grams of thiourea in an oil bath. The temperature of the mixture which at first melted to a deep red liquid was gradually raised. When the temperature reached 180° C. the reaction proceeded very rapidly with a considerable evolution of gas, the temperature in the
reaction mixture rising to 220° C. After maintaining the
temperature of the melt at 170-180° C. for an hour, the fused
product was dissolved in 200 cc. of 10% sodium hydroxide
solution by heating. On filtering into dilute hydrochloric
acid, a dark green amorphous powder precipitated which was
filtered off and taken up in hot alcohol. The alcoholic solu-
tion, acidified with hydrochloric acid, was allowed to stand
over night. A blue amorphous precipitate deposited which was
filtered off. From the filtrate the product was thrown down
as a grayish green precipitate by diluting with a large volume
of water. The α-sulfhydrylbenzimidazol was filtered off and
dried. It weighed 4 grams and melted at 295° C. as compared to
293-3° C. as reported by Kym.

The procedure as given by Gucci is as follows:
Orthophenylenediamine, 6 grams, carbon disulfide, 5 grams, and
10 cc. of absolute alcohol were heated in a bomb tube for 10
hours at a temperature of 120-140° C. On opening the cold tube,
a considerable pressure was released accompanied by a strong
odor of hydrogen sulfide. The reaction mixture consisted large-
ly of yellow crystals in the form of plates and flat needles.
These crystals were filtered from the mother liquor, washed
with alcohol and dried. The yield of α-sulfhydrylbenzimidazol
was 6 grams and the product, which started to soften at 290° C.,
melted at 296-7° C.
SUBSTITUTED DIPHENYLTHIOUREAS

Bis(ortho-chlorophenyl)thiourea.

Orthochloraniline, 30 grams, was poured into 100 cc. alcohol, 35 grams carbon disulfide added and the reaction mixture refluxed for 24 hours, but apparently no reaction had taken place. Pulverized potassium hydroxide, 10 grams, and 25 cc. more of carbon disulfide were added and the mixture refluxed for four hours. After cooling, the alcohol and excess carbon disulfide were distilled off and the residue washed with water and then with dilute hydrochloric acid and finally with water. The product crystallized from alcohol in the form of fine white needles, melting 135-6 C. The yield of bis-ortho-chlorophenylthiourea was 8 grams.

The analysis was as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>BaSO₄</th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>.2005 grams</td>
<td>.1603 grams</td>
<td>10.77%</td>
<td>10.97%</td>
</tr>
</tbody>
</table>

Grosch claims that bis(ortho-chlorophenyl)thiourea is not formed with ortho-chloraniline and carbon disulfide when heated in alcoholic potash. He states further that heating the above reagents in a sealed tube does not reduce the substituted thiourea. Grosch prepared bis(ortho-chlorophenyl)thiourea by the action of thiophosgen on orthochloraniline and obtained a product melting 141⁰ C.
Bis(meta-bromphenyl)thiourea.

Metabromaniline, 25 grams, was poured into 100 cc. of alcohol, 40 grams of carbon disulfide added and the solution refluxed for 15 hours. Potassium hydroxide, 10 grams, was then added and the mixture refluxed for 6 hours, when 25 cc. more of carbon disulfide was added. After refluxing, the reaction mixture 12 hours further, the alcohol and excess carbon disulfide were distilled off and the residue poured into water. The product, insoluble in water, was thoroughly washed first with water, then with dilute hydrochloric acid and finally with water. The product crystallized from dilute alcohol in long white needles which melted at 132-3°C. The yield of bis(metabromphenyl)thiourea was 18 grams. This compound is not described in the literature.

The analysis was as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>BaSO₄</th>
<th>Sulfur Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>.2010 grams</td>
<td>.1520 grams</td>
<td>8.29%</td>
<td>9.01%</td>
</tr>
</tbody>
</table>

Bis(ortho-iodophenyl)thiourea.

Orthoiodoaniline, 10 grams, and 6 grams of carbon disulfide were mixed with 10 cc. of a 20% solution of sodium hydroxide and 50 cc. alcohol added. The reaction mixture was refluxed for eight hours. It was noted that after the first three hours a few crystals separated which did not dissolve on further heating. These crystals were filtered off, washed
and dried, melting 165-70°C. To the solution, 10 grams more of carbon disulfide was added and the reaction mixture refluxed further for 22 hours. The solvents were distilled off and the residue washed with dilute hydrochloric acid and finally with water. The product on recrystallization from alcohol melted at 165.5°C to a red liquid. The yield of \( \text{bis[ortho-iodophenyl]thiourea} \) was only 4 grams. This compound has not been previously described. The analysis was as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{BaSO}_4 )</th>
<th>Sulfur Calculated</th>
<th>Sulfur Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.421</td>
<td>0.0664</td>
<td>6.66%</td>
<td>6.42%</td>
</tr>
<tr>
<td>1.860</td>
<td>0.0857</td>
<td>6.66</td>
<td>6.33</td>
</tr>
</tbody>
</table>

\( \text{Bis[para-ethoxyphenyl]thiourea} \)

Para phenetidin, 45 grams, was mixed with 50 grams of alcohol, 40 grams of carbon disulfide added and the mixture refluxed for six hours. On cooling, the crystal mass formed was filtered off and dissolved in 500 cc. benzene by heating. The product crystallized as white scales which were filtered off, washed with benzene and dried. The \( \text{bis[para-ethoxyphenyl]} \) thiourea weighed 45 grams and melted 172-3°C. The melting point recorded in the literature is given as 168°C.\(^\#\)

\(\#\) D. R. P. 66550
**Bis(ortho-methoxyphenyl)thiourea.**

Ortho anisidin, 40 grams, was stirred into 100 grams of alcohol, 40 grams of carbon disulfide added and the mixture refluxed for about fifteen hours. After cooling, the deposit of crystals was filtered off, dissolved in 300 cc. benzene by heating and the solution allowed to cool. The product, crystallized in coarse white needles, was filtered off, washed with benzene and dried. The bis(ortho-methoxyphenyl)thiourea weighed 32 grams and melted 139-140° C., as compared to 135° C. recorded in the literature. *\# D. R. F. 68706*

**Bis(para-aminophenyl)thiourea.**

Paraphenylenediamine, 20 grams, was dissolved in 200 cc. of alcohol and 35 grams of carbon disulfide added. A crystalline precipitate formed at once. The reaction mixture was refluxed for nine hours and, after cooling, the crystal mass filtered off, washed with alcohol and dried. The bis(para-aminophenyl)thiourea weighed 7 grams and melted 196° C. as compared with a melting point 195° C., previously reported. *\# D. R. F. 58204, 60182*
Diphenylparaphenylenedithiourea. \[ \text{C}_6\text{H}_4\text{NHC}_6\text{H}_5 \text{S} \text{NH} \text{C}_6\text{H}_4 \text{NH} \text{C}_6\text{H}_5\text{NH} \]

# Lellman, Ann. 221, 28

Paraphenylenediamminin, 6 grams, was dissolved in 200 cc. of alcohol by heating, the solution cooled somewhat and 18 grams of phenyl mustard oil in 50 cc. of alcohol slowly stirred in. Energetic reaction occurred and crystal mass deposited was filtered off, extracted twice with boiling alcohol and the residue dried. The product was in the form of small flakes, tinged a light purple and weighed 20 grams. The diphenylparaphenylenedithiourea sintered at 220° C. and melted at 230° C. which agrees with the melting point reported by Lellman.

Paraphenyleathyiourea. \[ \text{C}_6\text{H}_4\text{NH} \text{CS} \]

Diphenylparaphenylenedithiourea, 15 grams, were melted in a small pyrex flask on a sand bath. At a temperature of 200° C. and above, a white deposit formed on the walls of the flask. Finally the temperature was raised to 250° C. for an hour. After the melt had cooled it was finely pulverized and extracted three times with boiling alcohol. It was then pulverized again and extracted twice with ether. After drying, the paraphenylene thiovourea weighed 5 grams and melted 260-265° C. as compared to
the melting point of 270-271° C. reported by Lellman. #

# Ann. 221, 28

The reaction involved is as follows:

\[
\begin{align*}
\text{C=S} \quad & \quad \text{NHC}_6\text{H}_5 \\
\text{NH} \quad & \quad \text{C}_6\text{H}_4 \\
\text{NH} \quad & \quad \text{C=S} \\
\text{C=S} \quad & \quad \text{NHC}_6\text{H}_5 \\
\end{align*}
\]

\[
\begin{align*}
\text{heat} \quad & \quad \rightarrow \\
\text{C=S} \quad & \quad \text{NHC}_6\text{H}_5 \\
\text{C}_6\text{H}_4 \quad & \quad \text{NHC}_6\text{H}_5 \\
\text{NH} \quad & \quad \text{C=S} \\
\end{align*}
\]

Decomposition of Ammonium Phenylthiocarbamate.

Ammonium phenylthiocarbamate, 70 grams, was suspended in 500 cc. benzene and the mixture refluxed for thirty two hours. The solution after filtering and cooling deposited plate-like crystals. These were filtered off, washed with benzene and dried. The product weighed 10 grams and melted 150-152° C. The compound was believed to be diphenylthiourea and the following tests were made. A portion of the material was powdered with an equal amount of diphenylthiourea; the mixture melted 150-152° C.

The methyl derivative was also prepared as follows: The above compound, 3 grams, and 20 grams of methyl iodide were dissolved in 25 cc. absolute alcohol and the solution refluxed for a short time. The hydro iodide of the methyl derivative was then precipitated with ether and the crystal meal filtered off.
After drying, the crystals weighed 3.5 grams and melted 158-
160° C. The free methyl derivative was obtained by treating
the hydro iodide with sodium carbonate solution, and extracting
with ether. On recrystallization from alcohol, the product
melted sharply at 110° C, thus identifying it as the methyl
derivative of diphenylthiocurea. This fact confirms the identity
of the compound obtained above from the decomposition of
ammonium phenyldithiocarbaminate, as diphenylthiocurea. This also
confirms the work of Losanitch# and of Sebrell and Boord.
# Ber. 24, 3022 (1891); Ann. 166, 142.

Ammonium phenyldithiocarbazinate.

Phenylhydrazin, 21.6 grams, and 10 grams of aqueous
ammonium hydroxide was dissolved in 50 grams of alcohol and the
solution cooled externally in a freezing mixture. To the cooled
solution, 18 grams of carbon disulfide in 30 cc. ether was
added slowly with stirring. The reaction proceeded rapidly and
a pasty mass of white crystals deposited from the solution. After
standing half an hour, the crystals were filtered off, washed
with alcohol and ether and dried. The yield of ammonium phenyl-
dithiocarbazinate was 35 grams and the material melted 119.5° C.
as compared to 117.5° C. reported by Busch and Ridder#.
# Ber. 30, 845
Phenylhydrazonium phenyl dithiocarbazinate. \( \text{C}_6\text{H}_5\text{NHNH.C-SH\text{NH}_2.NHC}_6\text{H}_5. \)

Phenylhydrazine, 10 grams, was dissolved in 60 cc. ether, and to the strongly cooled solution 4 grams of carbon disulfide in 20 cc. ether was added slowly with stirring. A heavy precipitate deposited immediately. The reaction mixture was allowed to stand in the ice box for four hours, filtered, washed with ether and dried. The phenylhydrazonium phenyl dithiocarbazinate weighed 12 grams and melted 100-101\(^\circ\) C. as compared to 96-97\(^\circ\) C. reported by Fischer.

# Ann. 190, 114

Paraphenetethyl para-ethoxy phenyl dithiocarbamate. \( \text{C}_6\text{H}_5\text{O.C.NH.C-SH.NH}_2. \)

A solution of 27 grams of paraphenetidin in 100 cc. ether was cooled with ice and 15 grams carbon disulfide added slowly with stirring. A heavy white precipitate formed at once and was filtered off, washed with ether and dried. The paraphenetethyl para-ethoxyphenyl dithiocarbamate weighed 25 grams and melted 69-70\(^\circ\) C. This compound has been previously reported by Hugershoff.

# Ber. 32, (1899) 2245
Dicyan diamid salt of phenyldithiocarbamic acid.

\[ \text{C}_6\text{H}_5\text{NH}.\text{C}.\text{SH}.\text{NH}_2-\text{C}=\text{NH} \]

\[ \text{S} \quad \text{NHCN} \]

Dicyan diamid, 4 grams, was dissolved in 400 cc. alcohol and the solution filtered. Aniline 4.5 grams and carbon disulfide, 24 grams were added and the reaction mixture allowed to stand for a month. Large diamond shaped crystals formed and were filtered off, washed with dilute alcohol and dried. The product weighed 3 grams and melted sharply at 148° C.

Analysis:
TECHNICAL PART

THE VALUE OF DIPHENYLGUANIDINE, ITS DECOMPOSITION PRODUCTS
AND SULFUR DERIVATIVES AS ACCELERATORS OF VULCANIZATION.

With very few exceptions, all compounds described in
the first part of this paper have been tested to determine their
relative value as accelerators of vulcanization.

These derivatives were compounded in the following
stock formula and cured at 40°F steam pressure:

100.00 Rubber
5.00 Zinc oxide
6.00 Sulfur
1.00 Accelerator or equivalent molecular fractions
of homologous compounds.

Preliminary block cures were first obtained and from these the
optimum was judged by hand tests. Sheets were then made up on
all compounds which gave fair cures under two hours and the
physical tests run on these sheets. The tensile strengths are
reported in kilograms per square centimeter and the elongations
in per cent.

The tests obtained from the diphenylguanidine-sulfur
reaction product, tetraphenylmelamine, phenylcyanamid, phenyl-
cyranamid-ammonia, and phenylcyanamid-aniline were compared with
diphenylguanidine as shown graphically on sheet No. I. The data
from which these curves were drawn is given in Table I (page 56)
and the tests numbered 1 to 6 inclusive.
Since phenylcyanoamid contains one-half molecule of water of crystallization, 1.07 part of this accelerator was used in the standard formula. In order to determine whether any one of the decomposition products of diphenylguanidine might be responsible for its accelerating action, not only was each decomposition product tested but mixtures of these several products as well. Thus, a mixture containing an equivalent quantity of phenylcyanoamid and ammonia as well as one containing equal equivalents of phenylcyanoamid and aniline was compounded and the tensile strength determined on the cured stock.

The results may be briefly summarized:

1. No one of these decomposition products accelerates vulcanization to the same degree as diphenylguanidine.

2. The diphenylguanidine-sulfur reaction mixture gave an optimum cure in 90 minutes but the sheet showed a very low tensile strength. The conclusion to be drawn is that if an intermediate compound is responsible for the accelerating action of diphenylguanidine, it was destroyed under the conditions of fusion process.

3. Tetraphenylmelamine as shown in curve C gave an optimum cure in 90 minutes with a reasonably high tensile strength. Triphenyldicarbimid, another final decomposition product of diphenylguanidine, gave no cure under two hours. Apparently, the ultimate heat decomposition products of diphenylguanidine are not in themselves responsible for the speedy acceleration produced by diphenylguanidine.
4. One of the intermediate decomposition products of diphenylguanidine, phenylcyanamid, as shown on curve D proved to be only moderately fast in its accelerating action, the optimum cure being reached in 30 minutes. Curve E shows the maximum tensile strength obtained when a mixture of phenylcyanamid and ammonia was used and curve F when a mixture of phenylcyanamid and aniline was used. In both cases, the optimum cure was reached in 90 minutes, showing that by reducing the amount of phenylcyanamid from 1.07 parts to .6 parts with the addition of an equivalent of ammonia or aniline, the same ultimate effect is produced. The other primary heat decomposition product of diphenylguanidine, namely, diphenylcarbimid, gave no cure in two hours.

5. The conclusions drawn from the above results are:

First: that there is no stable product produced by the interaction of diphenylguanidine and sulfur under temperature and pressure conditions of vulcanization which exerts an accelerating action equal or greater than diphenylguanidine.

Second: that neither the ultimate or intermediate heat decomposition products of diphenylguanidine are responsible for its fast accelerating action.
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**Table I**

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**Notes:**
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- Part 2: 150
- Part 3: 150
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- Part 5: 150
- Part 6: 150
The accelerating action of diphenylguanidine sulfide
was compared with diphenylguanidine as shown graphically on
curve sheet No. II. The tabulated data is given in table No. II
(page 53), tests numbered 7 and 8. Diphenylguanidine sulfide
was compounded in the standard formula using 1.08 parts. These
two substances were powdered, passed thru a 100 mesh screen, com-
pounded on the mill for the same length of time and cured together
in the same press for each cure. The cured slabs showed a uniform
grain and were allowed to age over night before testing. Curves
A and B show the maximum tensile strength of each accelerator while
curves C and D are the tensile-elongation curves at the optimum
cure, 20 minutes. The conclusions to be drawn from these results
are as follows:

1. Diphenylguanidine sulfide, curve D, shows a higher maxi-
mum tensile strength thruout the middle portion of the curve, than
diphenylguanidine, curve A. The elongations correspond very closely.

2. The tensile-elongation, curve D, of diphenylguanidine sul-
fide at the optimum cure shows an accelerator of faster curing power
than diphenylguanidine, curve C.

3. The accelerating action of diphenylguanidine may be
ascribed to the formation of a hydrogen sulfide derivative, the sul-
fide, which may be formed at low temperatures and which liberates
the sulfur in active form, thus accelerating vulcanization.
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**TABLE II**

- Accelerator: 200, 300, 400, 500, 600, 700
- Tensile Performance: Cure, Flow, Tensile
- Cure Temp: 0 to 120° C
Curve Sheet No. II

Maximum Tensile Cure at 90°

Tensile - Time Curves

A. Diethyl Guanidine
B. Diphenyl guanidine Sulphide

Optimum Cure 30 min. at 40°

Tensile - Elongation Curves

C. Diphenyl guanidine
D. Diphenyl guanidine Sulphide

No. 290-F THE H. COLE CO., COLUMBUS, OHIO
The derivatives of dithiocarbamic acid tested included: diphenylguanidine salts of phenyldithiocarbamic acids, o-tolyl dithiocarbamic, p-tolyldithiocarbamic, p-methoxyphenyldithiocarbamic and phenyldithiocarbazinic acids. The data on these tests are shown graphically on sheet No. III which represents a summary of the maximum tensile strengths obtained. In these curves the tensile strength in kilograms per square centimeter has been plotted against time of cure. The data is given in table No. III (page 60) and the tests numbered 9 to 13 inclusive.

In every case the compound proved to be a fast curing accelerator, the optimum cure being reached in 15 to 20 minutes. Each curve rises sharply to a peak and then falls rapidly, indicating that the stock has been overcured. The p-methoxy derivative, Curve B, showed the highest maximum tensile strength in this series. The o-tolyl derivative, curve B, gave a greater maximum tensile strength than its homologue, the p-tolyl derivative, curve C. The phenyl derivative, curve A, showed a wide range, yielding about the same tensile strength but more slowly. The diphenylguanidine salt of phenyldithiocarbazinic acid, curve E, approximated very closely the same salt of p-tolyldithiocarbamic acid, curve C. The results may be briefly summarized as follows:

1. The curing power of this series of compounds is approximately the same.

2. The activity and the tensile strength reached at the optimum cure is no greater than in the case of diphenylguanidine.

3. This class of compounds shows a remarkable tendency to overcure rapidly beyond the optimum cure.
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<tr>
<th>TABLE III</th>
<th>Cure 100 200 300 400 500 600 700 Retention % at Test No.</th>
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*Note: The table and its content appear to be a mix of data and what seems to be a page from a book or a manual.*

---

**Table Description:**

- **Table Title:** TABLE III
- **Column Headers:** Cure 100 200 300 400 500 600 700 Retention % at Test No.
- **Rows:**
  - **Part I:** Percentage Retention at various test numbers.
  - **Part II:** Percentage Retention at various test numbers.
  - **Part III:** Percentage Retention at various test numbers.
  - **Part IV:** Percentage Retention at various test numbers.
  - **Part V:** Percentage Retention at various test numbers.
  - **Part VI:** Percentage Retention at various test numbers.
  - **Part VII:** Percentage Retention at various test numbers.
  - **Part VIII:** Percentage Retention at various test numbers.
  - **Part IX:** Percentage Retention at various test numbers.
  - **Part X:** Percentage Retention at various test numbers.

**Notes:**

- The table seems to be part of a larger document, possibly a manual or a research report.
- The data is presented in a tabular format with test numbers ranging from 1 to 10.
- The percentage retention is likely related to some form of test or analysis, possibly in a scientific or technical context.
The accelerating action of triphenylguanylthiourea, triphenylguanidine, diphenylguanidine mercaptobenzothiazol and the reaction product of diphenylguanidine with carbon disulfide were compared with diphenyl guanidine and the results are shown graphically by the curves on sheet No. IV. Diphenylguanidine mercaptobenzothiazol proved to be so fast in its accelerating action that a test was also made in which only .5 part of this accelerator was compounded in the standard formula. The complete data is given in table No. IV (page 65) and the tests numbered 14 to 19 inclusive.

From a study of these curves the following conclusions may be drawn:

1. A marked difference is apparent in the curing power of diphenyl and triphenylguanidine (curves A and D). The diphenylguanidine is about six times as fast and develops a far superior tensile strength.

2. The carbon disulfide-diphenylguanidine reaction product gave a fast curing stock although not as active as diphenylguanidine while the tensile strength fell below that of diphenylguanidine and the stock was badly overcured.

3. Triphenylguanylthiourea, curve C, gave a comparatively slow curing stock about one-third as active as diphenylguanidine and with a tensile strength much lower.
4. Diphenylguanidine mercaptobenzothiazol, when compounded
gave a stock of extraordinarily fast curing power. In the com-
 pound prepared by using 1 part of this derivative, the optimum
cure was judged to be about 5 minutes at 40# steam pressure.
The results obtained by compounding only .5 part of the same
substance are shown in curve E and indicate more clearly the
pronounced accelerating action of this substance. The optimum
cure is reached in 30 minutes, after which time the stock rapidly
overcures. Apparently this compound combines the rapid
accelerating action of mercaptobenzothiazol and diphenylguanidine
but produces rapid overcuring under these conditions.
Tests on Miscellaneous Compounds.

The results of the tests on phenyldithiobiiazolon thiol and thiobiiazoldisulfhydride are shown graphically on sheet No. V. The data for these tests is given in table No. V (page 63), and the tests are numbered 20 and 21. For these two compounds the tensile-time curves have been plotted and also the tensile-elongation curves at the optimum cure in each case. The compounds α-sulphydryl benzimidazol and 1-phenyl-2-phenylimido-5-thio-3,4-disulfazolidin were also tested but gave no cure under two hours. The following conclusions may be noted:

1. The curing power of these two compounds is approximately the same. The compound containing thiobiiazoldisulfide gave a cure of high tensile strength, superior to that given by the one containing phenyl-dithiobiiazolon-thiol.

2. The optimum cure in the case of phenyldithiobiiazolon thiol was found to be at 120 minutes and of thiobiiazoldisulfhydride at 105 minutes. When plotted the curves are nearly coincident.

3. It was originally believed both of these compounds would prove to be very fast accelerators due to the sulfur groups present. Particularly in the case of thiobiiazoldisulfhydride which contains a double mercapto thiazol group

\[ \begin{align*}
N & - N \\
\text{HS-C} & \text{S-C-SH}
\end{align*} \]
one should expect an accelerating action comparable to 1-mercaptobenzothiazol. The results seem to indicate that the \(-S-C-SH\) group is not all that is required in a good accelerating agent.
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**TABLE A**
The results of the tests on: bis-p-aminophenyl thiourea, phenetyl ammonium ethoxyphenyl-dithiocarbamate, bis(p-ethoxyphenyl)thiourea, phenylhydrazonium phenyldithiocarbamate are grouped together on sheet No. VI. The data for these tests is given in table No. VI (page 68) and the tests numbered 22 to 25 inclusive.

The following conclusions may be noted briefly:

1. The dithiocarbamic acid derivative prepared from p-phenetidine gave the highest tensile of any of the compounds of this group and showed a greater activity than the corresponding disubstituted thiourea and a much higher tensile. The tendency to overcuring characteristic of the dithiocarbamates is evident here also.

2. Curves A and C of bis(p-aminophenyl)thiourea and bis(p-ethoxyphenyl)thiourea show stocks of approximately the same curing power.

3. Phenylhydrazonium phenyldithiocarbamate gave a stock of low curing power and poor tensile which rapidly overcured beyond the optimum point. The dithiocarbamic acid derivative gave the slowest curing stock of any dithiocarbamate tested.

4. Diphenyl-p-phenylenedithiourea and p-phenylene thiourea, bis(-o-chlorophenyl) thiourea, bis(-o-dimethoxyphenyl) thiourea, bis(m-dibromophenyl) thiourea showed no cure at 2 hours.
THE MECHANISM OF ACCELERATION BY DIPHENYL GUANIDINE

Diphenylguanidine, because of the tautomeric hydrogen atom, may exist in either the amino or imino forms:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NH} & \leftrightarrow \text{C}_6\text{H}_5\text{NH}^+ \\
\text{C}_6\text{H}_5\text{NH} & \leftrightarrow \text{C}_6\text{H}_5\text{N}^+ \text{C} - \text{NH}_2
\end{align*}
\]

Symmetrical trisubstituted guanidines can exist in only one form since the tautomers would be identical. In support of this point, Larckveld\(^a\) has shown that diphenyl tolyl guanidine prepared from thiocarbanilid and p-toluidine is identical with that prepared from phenyl-p-tolylthiourea and aniline.

Keith and Schroeder\(^b\) advanced evidence of the existence of the imino form for disubstituted guanidines. They based their conclusions upon the fact that the imide would react with carbon disulfide to produce thiocarbanilid and thiocyanic acid, while the amide would yield phenyl mustard oil and phenyl thiourea. Scott\(^c\) has pointed out that it is just as reasonable to assume that the amide would react with carbon disulfide to produce thiocarbanilid and thiocyanic acid, thus:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NH} & \Rightarrow \text{C}_6\text{H}_5\text{NH}^+ + \text{CS}_2 \\
\text{C}_6\text{H}_5\text{N}^+ \text{C} - \text{NH}_2 & \Rightarrow \text{C}_6\text{H}_5\text{N}^+ \text{C} - \text{NH}_2 + \text{HSCN}
\end{align*}
\]
We have found that the reaction of diphenylguanidine and carbon disulfide probably takes place with intermediate formation of a dithiocarbamate, as in the case of other amines, subsequently decomposing to give thiocarbanilide and thiocyanic acid.

Rathke and Oppenheim have reported other reactions which they attribute to the amino form of diphenylguanidine. They found that phenyl mustard oil acting on diphenylguanidine at room temperature, yielded triphenylguanithiourea and that phenyl cyanamid

\[
\text{C}_6\text{H}_5\text{N} - \text{C} = \text{NCH}_2 + \text{C}_6\text{H}_5\text{NCS} \rightarrow \text{C}_6\text{H}_5\text{N} - \text{C} = \text{NCH} - \text{CS} - \text{NHC}_6\text{H}_5
\]

reacts in a similar way with diphenyl guanidine to form tri-phenyl biguanide.

\[
\text{C}_6\text{H}_5\text{N} - \text{C} = \text{NH}_2 + \text{C}_6\text{H}_5\text{NHC} = \text{N} \rightarrow \text{C}_6\text{H}_5\text{N} - \text{C} = \text{NH} - \text{C} = \text{NHC}_6\text{H}_5
\]

Scott has shown that diphenyl carbimid reacts with diphenylguanidine to form the base, tetraphenyl biguanide.

\[
\text{C}_6\text{H}_5\text{N} - \text{C} = \text{NH}_2 + \text{C}_6\text{H}_5\text{N} = \text{C} = \text{N} \rightarrow \text{C}_6\text{H}_5\text{N} - \text{C} = \text{NH} - \text{C} = \text{NHC}_6\text{H}_5
\]

Additional evidence has been advanced by Scott, who has shown that diphenylguanidine reacts with hydrogen sulfide and carbon disulfide yielding diphenylguanidine trithiocarbonate.

\[
\text{C}_6\text{H}_5\text{NH} - \text{C} = \text{S} - \text{C} - \text{S} - \text{N} - \text{C} \quad \text{H}_3 - \text{NHC}_6\text{H}_5
\]
It was first shown by Hoffman\(^\#\) that carbon disulfide reacts with diphenylguanidinidine to give thiocarbanilid and diphenylguanidine thiocyanate. Assuming that the diphenylguanidine salt of diphenylguanyldithiocarbamic acid is first formed, Scott has devised the following mechanism for the reaction:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{NH} & \quad \text{NH}_2\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5\text{N} & \quad \text{NHC}_6\text{H}_5 \\
\text{S} & \quad \text{H}_3 & \quad \text{I}_2 & \quad \text{H}_2\text{S} & \quad \text{NCSN-C} \\
\text{NCO}_6\text{H}_5 & \quad \text{C}_6\text{H}_5\text{N} & \quad \text{NC}_6\text{H}_5
\end{align*}
\]

The diphenylguanidine salt of diphenylguanyldithiocarbamic acid decomposes into diphenylcarbimid, hydrogen sulfide and diphenylguanidine thiocyanate. The diphenylcarbimid and hydrogen sulfide immediately react to form thiocarbanilid, thus accounting very satisfactorily for the final reaction products.

Bedford and Schaeffer\(^\#\#\) describe the product obtained from the reaction of one molecule of aniline, carbon disulfide, and diphenylguanidine, but ascribe an incorrect formula to the compound. Scott points out that the compound formed is the diphenylguanidine salt of phenyldithiocarbamic acid which has the formula:

\[
\begin{align*}
\text{S} & \quad \text{NHC}_6\text{H}_5 \\
\text{C}_6\text{H}_5\text{NH-C-S-H-C} & \quad \text{NCO}_6\text{H}_5
\end{align*}
\]

The heat decomposition products of this substance are phenyl mustard oil, hydrogen sulfide and diphenylguanidine. The mustard oil and the diphenylguanidine combine to give triphenyl
guanyl thiourea.

The logical conclusion drawn is that diphenyl guanidine exists in two tautomeric forms of which the amino form is largely responsible for the formation of sulfur derivatives.

The ultimate decomposition products of diphenylguanidine are ammonia, aniline, tetraphenylmelamine and triphenyl dicarbimid. This is best explained upon the assumption that the imino form of diphenylguanidine yields aniline and phenyl cyanamid, while the amino form yields ammonia and diphenyl carbimid. Phenyl cyanamid and diphenyl carbimid react mole for mole to yield triphenyl dicarbimid:

\[
\text{C}_6\text{H}_5\text{NH}_2\text{CN} + \text{C}_6\text{H}_5\text{N}=\text{C}=\text{NC}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{N}=\text{C}=\text{NC}_6\text{H}_5
\]

while in the proportions of two to one these same reagents combine to form tetraphenylmelamine

\[
2\text{C}_6\text{H}_5\text{NH}_2\text{CN} + \text{C}_6\text{H}_5\text{N}=\text{C}=\text{NC}_6\text{H}_5 \rightarrow \text{C}_6\text{H}_5\text{NH}\text{C}=\text{NC}_6\text{H}_5
\]

On testing these derivatives for their activity as accelerators no single decomposition product or combination of such products were found which accelerated the process of vulcanization to the same degree as diphenylguanidine. The effect of combining the components brought out the interesting fact that if the amount
of phenyl cyanamid was cut down to one equivalent, based on the molecular weight of diphenylguanidine, and compounded with equivalent amounts of ammonia or aniline respectively the optimum cure remained the same as when the larger amount of phenyl cyanamid was used. Attempts to isolate a pure sulfur derivative from the fusion mixtures of phenyl cyanamid and sulfur as well as diphenyl carbimid and sulfur were unsuccessful.

The conclusion to be drawn from these results is that the accelerating action of diphenylguanidine can be only partially accounted for on the basis of its primary decomposition products. The two most active components are ammonia and phenyl cyanamid.

The possibility that sulfur reaction products of diphenylguanidine were formed in the vulcanization process was suggested by the work done in the isolation of 1-mercaptobenzothiazole from the reaction between thiocarbamid and sulfur. The fusion mixture prepared from diphenylguanidine and sulfur, yielded only two substances susceptible of purification, tetraphenylmelamine and aniline. It proved impossible to isolate any product containing sulfur. The accelerating power of the crude fusion mixture was considerably lower than the original diphenylguanidine. It was, in fact, approximately equal to that of tetraphenylmelamine alone so it is safe to assume that this compound was responsible for the acceleration noted. The conclusion naturally follows that any sulfur derivative of diphenylguanidine
produced under conditions of vulcanization is not sufficiently stable to admit of its isolation.

Since it has been rather definitely shown that the amino form of diphenylguanidine permits it to act as a primary amine, the chemistry of diphenylguanidine must be closely analogous to that of ammonia. The very striking property exhibited by diphenylguanidine in forming salts of the various dithiocarbamic acids and with certain compounds containing mercapto groups, leads to the plausible assumption that there should exist a hydrosulfide, sulfide or polysulfides analogous to those formed by ammonia. Our observations lead us to believe that diphenylguanidine does form a very unstable hydrosulfide which as yet has not been isolated. The sulfide of diphenylguanidine, however, has been isolated and is herein observed for the first time. The formation of this sulfide is explained by assuming that two molecules of the hydrosulfide react with the loss of hydrogen sulfide.

Diphenylguanidine sulfide when compounded on an equivalent basis shows a somewhat higher acceleration value than diphenylguanidine. The logical conclusion is that this sulfide is the intermediate active agent responsible for the accelerating action of diphenylguanidine. This conclusion would definitely place diphenylguanidine as a "hydrosulfide" accelerator as previously stated by Scott and Bedford and also by Bedford and Sebrell

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who classified it as a "hydrogen sulfide polysulfide." accelerator.

Our conclusions are then entirely in agreement with the assumptions of these previous investigators as regards the classification of diphenylguanidine as an accelerator. These authors, however, failed to offer quantitative experimental evidence in support of their contention. The isolation of diphenylguanidine sulfide and its relative activity as an accelerator are offered as direct experimental proof in support of the conclusion that diphenylguanidine is a "hydrogen sulfide" accelerator.
SUMMARY AND CONCLUSIONS.

1. The chemistry of the decomposition of the ammonium and diphenylguanidine salts of phenyl dithiocarbamic acid has been investigated, and previous work verified.

2. A number of derivatives of the substituted diphenyl thioureas have been prepared, of which bis(-o-iodophenyl) thiourea and bis(-m-bromphenyl) thiourea have been described for the first time.

3. Fifteen new diphenylguanidine salts of the substituted phenyl dithiocarbamic acids, have been prepared. The diphenylguanidine salt of phenyl dithiocarbizinic acid as well as its salt of 1-mercaptobenzothiazole have been described for the first time.

4. A new synthesis of 1-mercaptobenzothiazole has been found.

5. A miscellaneous number of compounds including phenyl dithiobenzolothiol, thiobiazol disulfhydrate, α-sulphydrylbenzimidazol, and 1-phenyl-2-phenylimido-5-thio5,4-disulfazolidin have been prepared, and used to study the accelerating action of certain sulfur groups upon the process of vulcanization.

6. The heat decomposition products of diphenylguanidine, namely, tetraphenylmelamine, triphenylidicarbimid, phenylcyanamid and diphenylcarbimid have been prepared and their properties investigated.
7. The reaction mixture resulting from the fusion of diphenylguanidine and sulfur has been investigated and two pure compounds, tetraphenylmelamine and aniline, isolated from it.

8. Diphenylguanidine sulfide has been prepared and described for the first time.

9. The heat decomposition products of diphenylguanidine have been tested to ascertain their curing power. From the results, it can be stated that the primary accelerating action of diphenylguanidine may only partially be attributed to its decomposition products.

10. The fusion mixture resulting from diphenylguanidine and sulfur has been tested for its acceleration value and showed a much lower curing power than diphenylguanidine.

11. The curing power of diphenylguanidine sulfide was appreciably greater than free diphenylguanidine.

12. The final conclusion reached was that the acceleration of vulcanization by diphenylguanidine depends upon the formation of diphenylguanidine sulfide which is the active agent in accelerating the vulcanization process. This at once classifies diphenylguanidine as a "hydrosulfide" accelerator.

13. The diphenylguanidine salts of the substituted phenyl dithiocarbamic acids and of phenyl dithiocarbizinic acid have
been tested to determine their curing power. They proved to be very fast accelerators. The diphenylguanidine salt of 1-mercaptobenzothiazole has the highest curing power of any of the compounds tested, but rapidly overcured beyond the optimum point.

14. Phenyl dithiobiazolonthiol and thiobiazol disulf-hydrate have been tested, but showed only moderate curing power, although they both contain the \( \text{S}^-\text{C-SH} \) group. These results do not bear out the contention of Sebrell and Boord as well as Bruni and Romani who ascribed the peculiar accelerating action of 1-mercaptobenzothiazole to this group. The compounds, 1-phenyl-2-phenylimido-5-thio-3,4-disulfazolidin and \( \alpha \)-sulf-hydryl benzimidazol showed practically no activity as accelerators.
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AUTobiography

I, E. N. Cole Coolidge, was born at East Hartford, Connecticut, June 25th, 1897. My elementary and secondary education was received in the public school and high school of Boulder, Colorado and my first two years of undergraduate college training at the University of Colorado. I received the Bachelor of Arts degree from the Ohio State University in 1920, and in 1921 I was granted the degree of Master of Science by the same institution. In 1918, I entered the employ of The Falls Rubber Company as chemist, holding this position until October, 1919, when I returned to the Ohio State University. In the summers of 1920 and 1921, I was employed by The Dow Chemical Company as a research chemist. I returned to the Ohio State University in September, 1921, and completed the requirements for the degree of Doctor of Philosophy in the summer of 1923.