

Some Reactions Between Phenol and Hexamethyltetramin

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PHENOL AND
HEXAMETHYLTETRAMIN

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A Thesis

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of the Chemical Engineering School
of the University of Kansas.

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Candidate for the Degree of Bachelor of Science.

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PREFACE.

The following thesis is a review of my work carried out during the last four months under the direction and advice of Dr. Redman of the Industrial Department of the University of Kansas.

The work covers an entirely new field of investigation. My research is not more than just a start, the problems and possibilities arising each day were too numerous to follow up in my limited time, but an effort was made to start a systematic research and open up a field for more extensive work for anyone who cares to continue the work.

That part of the paper relating to the physical properties of the varnish, was written by Dr. Redman who took my manufactured materials and tested them for their physical possibilities.

W.E. Vawter.

SOME REACTIONS OF PHENOL AND HEXAMETHYLTETRAMIN.

For many years a reaction has been known between phenol and formaldehyde. Many complicated products have been obtained, according to the conditions of the experiment or the kinds and quantities of the reacting materials used. The reaction was only of a theoretical interest and no uses were made of the products for industrial purposes until of a very recent period.

Arthur Smith (Eng. Pat. No 16247, Aug. 9, 1899., cited from Jr. Soc. Chem. Ind., Nov. 30., 1899, page 1029.) obtained a product by mixing acetic aldehyde with methylated spirits, phenol and fused oil, or methylated spirits which had been saturated with hydrochloric acid or sulphuric acid, the product obtained was molded and used for electrical insulations.

A Luft (Eng. Pat. No 10218, May 3, 1902. Cited from Jr. Soc. Chem. Ind., Aug. 30, 1902.) mixed 100 parts of phenol and 100 parts of formaldehyde of 50% strength with 40 to 80 parts of a 16% solution of sulphuric acid. A white viscous mass was obtained, addition of glycerine, alcohol or camphor in solution made it more plastic. This material was not attacked by hot acids or alkalis.

E. M. Raetz (Eng. Pat. No 27889, Dec. 19, 1903., Cited from Jr. Soc. Chem. Ind., May 16, 1904, page 500.) mixed in an autoclave a solution of phenol and soap with a 10% solution

of formaldehyde and a small quantity of alkali. The mixture was heated to 150 degrees Centigrade and then cooled. A solid product soluble in water was obtained. The solution was used as an antiseptic.

E. H. Fayolle (Fr. Pat. No 341013 March 7, 1904, Cited from Jr. Soc. Chem. Ind., Sept. 15, 1904, page 873.) obtained a material by the interaction of glycerine, strong sulphuric acid, formaldehyde and phenol. The material obtained was wax like, soluble in alcohol. It was suitable for varnish making and substitute for caoutchouc.

A Stephen (Fr. Pat. No 345398 Aug. 6, 1904. Cited from Jr. Soc. Chem. Ind. Dec. 31, 1904, page 1233.) heated 200 grams of phenol with 400 grams of 40% solution of formaldehyde in the presence of an alkali under a reflux condenser to a temperature of 100 degrees Centigrade until the odor of phenol had disappeared. A precipitate formed which was dried and used for a disinfectant.

W. H. Story (Eng. Pat. No 8875 April 27, 1905. Cited from Jr. Soc. Chem. Ind. Oct. 31, 1905, page 1081.) obtained a product by using the same materials and boiling under a reflux condenser for eight hours. When the product was warm it could be molded or it could be dissolved in an organic solvent and used as a varnish, but if it is allowed to cool the material is soluble in nothing and is not even attacked by alkalis or acids excepting fuming nitric acid.

L. Heim (Eng Pat. No 25216 Nov. 13, 1907. Cited from

Jr. Soc. Chem. Ind. April 30, 1908, page 412.) obtained a substitute for resin by heating phenol and formaldehyde with aniline. The condensing agent could be any amine or ammonium salt.

L. H. Baekeland (Jr. Ind. Eng. Chem. March 1909, page 149.) produced a product which he called Bakelite. This substance was made by heating equal parts each of phenol and formaldehyde with a small quantity of some alkaline condensing agent. He was able to obtain three products, representing three different points of the entire reaction. The first product he called Bakelite A, which is a liquid, viscous or pasty or it may be a solid; it is soluble in alcohol, acetone, phenol, and glycerine. The next product he called Bakelite B which was formed by continued heating of A; this material is a solid at all temperatures, if heated it softens and becomes rubber-like, it is insoluble in all solvents but may swell in acetone or phenol, continued heating changes it into the final product called Bakelite C. The C product is infusible and insoluble in all solvents, unattacked by acetone, acids or alkaline solutions, concentrated sulphuric acid destroys it but the dilute acid will not. Up to a temperature of 300 degrees Centigrade no change takes place in the material but above this temperature it will char without fusing.

Baekeland explains that difference in these products is due to the amount of water in them, A having the most and

as A is heated water is driven off until B is formed, continued heating drives off the rest of the water and C is then formed.

There are a number of other patents for products obtained by the reaction of a phenol or a phenolic body upon an aldehyde or some polymerized form of an aldehyde. Every patent calls for some condensing agent to accelerate the reaction. The inventors do not agree very well as to what temperatures to use, the temperatures vary from 50 to 180 degrees Centigrade. The majority of the inventors appear to favor a temperature close to 100 degrees Centigrade..All patents require a reflux condenser during the progress of the reaction.

The composition of all these products and the reaction which takes place is not known. Baekeland goes to great trouble in bringing forward a theory that it is a polymerized oxybenzyl-methylen glycol-anhydride, since one mole of formaldehyde and six moles of oxybenzylalcohol react and give a material similar to bakelite in its physical properties and also in its chemical analysis. In all the reactions water is formed and must be contended with.

The reaction between hexamethyltetramin and phenol is similar to the reaction between formaldehyde and phenol. Moschatos and Tollens (Ann. 272, 280.) found that when phenol and hexamethyltetramin were mixed and warmed, that when they cooled compound separated in crystalline form, which on being

analysed gave the formula represented by the symbols $(C_6H_{12}N_4)3(C_6H_5OH)$. These crystals were decomposed between 115 and 124 degrees Centigrade, and according to their paper the decomposition product had the odor of fish. Dry distillation gave a product of the odor of phenol and ammonia. When their product was heated with dilute sulphuric acid the distillate had the odor of phenol and formaldehyde, on cooling the mass became gelatinous.

When phenol and hexamethyltetramin are added together and heated, a reaction takes place which results in a transparent, yellowish, resinous or amber like mass and this mass may be a solid or liquid depending on the length of time and degree of heating. The presence of an organic solvent may vary the reaction, the resulting product being a varnish.

When phenol and hexamethyltetramin are used, no condensing agents are required, as when phenol and formaldehyde are taken, no water is present and no water is formed during the reaction. A reflux condenser is required only when organic solvents are used to recondense the solvent.

The proportions of the reacting materials should be seven moles of phenol to one of hexamethyltetramin. The volume of the solvent should equal the volume of the phenol in the mixture. Six moles of phenol and one mole of hexamethyltetramin can be used, as was latter found with out any noticeable change in the product. The solvent was varied by using alcohol alone, alcohol and 5 to 10 percent of nitrobenzene, aniline, or

glycerine. Aniline, nitrobenzene, amyl alcohol, and phenol were also used as solvents in place of the alcohol.

The following formulas were used in the preparation of the different materials:-

Formula 1.

Phenol -----	400 grams.
Hexamethyltetramin -----	85 grams.
Alcohol 95% -----	375 C.C.

Formula 2.

Phenol -----	400 grams.
Hexamethyltetramin -----	85 grams.
Alcohol 95% -----	375 C.C.
Glycerine -----	15 grams.

Formula 3.

Phenol -----	400 grams.
Hexamethyltetramin -----	85 grams.
Alcohol 95% -----	375 c. c.
Nitro-benzene -----	30 grams.

Formula 4.

Phenol -----	400 grams.
Hexamethyltetramin -----	85 grams.
Alcohol 95% -----	375 c.c.
Aniline -----	30 grams.

Formula 5.

Phenol ----- 160 grams.
Hexamethyltetramin ----- 40 grams.
Amyl alcohol ----- 150 c.c.

Formula 6.

Phenol ----- 60 grams.
Hexamethyltetramin ----- 15 grams.
Phenol ----- 210 grams.

Formula 7.

Phenol ----- 60 grams.
Hexamethyltetramin ----- 15 grams.
Nitro-benzene ----- 66 grams.

Formula 8.

Phenol ----- 60 grams.
Hexamethyltetramin ----- 15 grams.
Aniline ----- 130 grams.

Formula 9.

Phenol ----- 400 grams.
Hexamethyltetramin ----- 85 grams.

Formula 10.

Phenol ----- 80 grams.
Hexamethyltetramin ----- 20 grams.
Amyl alcohol ----- 300 c.c.

The reacting products were placed in a flask and connected to a reflux condenser, the ammonia which passed off during the reaction was lead from the condenser to a vessel in which was some water. This water was neutralized by a standard solution of hydrochloric acid with litmus as an indicator. Curves were then made from the data obtained,

The flasks containing the alcohol solution, alcohol and glycerine, alcohol and nitro-benzene and alcohol and aniline were heated on a water bath until all the ammonia appeared to have come over. The flask containing the amyl alcohol solution was started on the water bath and after all the ammonia was over which was formed at that temperature, it was then placed on a wire gauze and the solution brought to boiling. All the other experiments were carried out on the oil bath.

The products obtained by using alcohol, alcohol and glycerine, alcohol and nitro-benzene, and alcohol and aniline as solvents, gave a product at the end of the reaction which was a transparent yellow colored liquid. Seven to nine hours are required to carry out the experiment, excepting the alcohol and aniline solution which only required five hours. The total quantity of ammonia which came off of the four solutions appears to be about the same with the exception of the aniline solution which is a little more than the others. The rate at which the ammonia comes off the solutions is higher during the second, third, fourth and fifth hours

than during the first hour or any time after the fifth hour. After 46% of the ammonia had come off of the solutions, the rate at which the ammonia came off dropped to zero and the reaction was complete. These solutions were at no time boiling, all the solutions had a temperature of 90 degrees except the alcohol and glycerine which had a temperature of 78 degrees Centigrade.

The amyl alcohol solution was placed on the water bath and heated, after replacing the water bath with a wire gauze the temperature was raised to the boiling point of the solution, 138 degrees Centigrade. The rate at which the ammonia came off, on the water bath, was slower than the other solutions but when the flask was placed on the wire gauze the rate increased greatly. The total amount of ammonia which came off was 12% percent larger than the other solutions. The total amount of ammonia which came off was not measured for when 58% of the ammonia had come off the mixture in the flask began to foam filling the flask, forcing the discontinuance of the heating. The resulting mass while hot was a yellow transparent color of a gelatinous nature, on cooling the mass became opaque yellow, hard and brittle with a strong odor of amyl alcohol.

The above reaction was repeated, the amount of amyl alcohol was doubled and the amount of phenol and hexamethylenetetramine was reduced each one half. The solution was heated to boiling at the start, 132 degrees Centigrade. For two hours

the ammonia came off steadily, at the end of the third hour the transparent liquid became cloudy which was followed by a precipitate settling out and collecting together and causing trouble in bumping. The clear solution became cloudy and began to bump within five minutes. Boiling was continued for 60 hours. The rate at which the ammonia came off after the precipitate settled was very small. The ammonia which came off was almost the entire ammonia content of the hexamethyltetramin. The precipitate which settled out was insoluble and infusible and on heating it charred, the solid substance obtained from the previous experiment of the amyl alcohol solution was likewise insoluble and would char on heating to high temperatures.

Phenol and hexamethyltetramin were mixed without any solvent and heated to boiling. The greater part of the ammonia which came off did so in 30 minutes, at the end of this time the thick viscous liquid began to foam and fill the flask. The flame was removed and the porous mass allowed to cool. The product was a clear yellow transparent substance, it was insoluble. On further heating it charred with the odor of burnt sugar.

In three of the experiments alcohol as a solvent was discontinued and in its place aniline, nitro-benzene and phenol were used as solvents.

The experiment where phenol was used as a solvent the

entire nitrogen content of the mass was given off as ammonia. The ammonia all came off within thirty minutes. The final product was a yellow transparent liquid and on standing the liquid turned to a transparent red; the liquid became partly solid on cooling due to the phenol crystallizing out.

The experiment with nitro-benzene as a solvent did not do so well. The reaction had just started when the mass became viscous and began to foam and the experiment was discontinued. The product was insoluble and had a strong odor of nitro-benzene.

The experiment with aniline as a solvent was then carried out. One volume of phenol had two volumes of aniline as a solvent. The entire amount of ammonia which came over did so within 30 minutes. The contents of the flask was boiled for 6 hours without any more ammonia coming off. The final product was a transparent yellow colored liquid.

In all the above experiments it was noticed that as the mixtures were heated that the hexamethyltetramin passed gradually into solution. As it passed into solution the liquid changed from a clear transparent to a yellow transparent; as soon as it had passed into solution the ammonia would begin to come over.

In all these experiments duplicates were run and they checked each other in a fairly satisfactory manner.

ANALYSIS OF VARNISHES.

Formula 1.

	<u>No.1</u>	<u>No.2</u>
Phenol-----	400.505 grams.	401.299 grams.
Hexamethyltetramin -----	85 .106 grams.	86.106 grams.
Alcohol -----	303.750 grams.	303.750 grams.
Ammonia Content -----	41.337 grams.	41.337 grams.
Ammonia driven off -----	18.765 grams.	18.750 grams.
Percent -----	45.39 %	45.36 %
Temperature of reaction --	90 degrees	89 degrees.

Formula 2.

Phenol -----	404.655 grams.	396.483 grams.
Hexamethyltetramin -----	86.060 grams.	84.595 grams.
Alcohol-----	307.000 grams.	300.500 grams.
Glycerine -----	14.955 grams.	15.279 grams.
Ammonia content -----	41.799 grams.	41.088 grams.
Ammonia driven off -----	19.161 grams.	18.991 grams.
Percent-----	45.84 %	46.22 %
Temperature of reaction ---	78 degrees.	78 degrees.

Formula No3.

	<u>No.1</u>	<u>No.2</u>
Phenol -----	400.331 grams.	400.879 grams.
Hexamethyltetramin -----	85.106 grams.	85.106 grams.
Alcohol -----	303.750 grams,	303.750 grams.
Nitro-benzene -----	30.455 grams.	30.515 grams.
Ammonia content -----	41.337 grams.	41.337 grams.
Ammonia driven off -----	18.825 grams.	19.100 grams.
Percent -----	45.30 %	46.20%
Temperature of the reaction	91 degrees.	88 degrees.

Formula 4.

Phenol -----	400.133 grams.	400.726 grams.
Hexamethyltetramin -----	85.106 grams.	85.106 grams.
Alcohol -----	303.750 grams.	303.750 grams.
Aniline -----	30.525 grams.	25.790 grams.
Ammonia content -----	41.337 grams.	41.337 grams.
Ammonia driven off -----	20.197 grams.	20.377 grams.
Percent -----	48.64 %	49.29 %
Temperature of the reaction	91 degrees.	91 degrees.

Formula 5.No.1No.2

Phenol -----	160.392 grams.	161.246 grams.
Hexamethyltetramin -----	40.003 grams.	40.003 grams.
Amyl alcohol -----	150.000c.c.	150.000 c.c.
Ammonia content -----	19. 50 grams.	19.500 grams.
Ammonia driven off -----	11.306 grams.	11.530 grams.
Percent -----	57.98 %	59.03 %
Temperature of reaction ---	138 degrees.	138 degrees.

Formula 6.

Phenol -----	270.080 grams.	271.057 grams.
Hexamethyltetramin -----	15.000 grams.	15.000 grams.
Ammonia content -----	7.285 grams.	7.285 grams.
Ammonia driven off -----	7.340 grams.	7.3000grams.
Percent -----	100.40 %	100.00 %
Temperature of the reaction	179 degrees	179 degrees.

Formula 7.

	<u>No.1.</u>	<u>No.2</u>
Phenol -----	60.220 grams.	59.948 grams.
Hexamethyltetramin -----	15.000 grams.	15.000 grams.
Nitro-benzene -----	66.330 grams.	67.057 grams.
Ammonia content -----	7.285 grams.	7.285 grams.
Ammonia driven off -----	3.000 grams.	3.000 grams.
Percent -----	41.10 %	41.10 %
Temperature of reaction --	203 degrees.	203 degrees.

Formula 8.

Phenol -----	59.993 grams.	60.716 grams.
Hexamethyltetramin -----	15.000 grams.	15.000 grams.
Aniline -----	126.780 grams.	129.300 grams.
Ammonia content -----	7.285 grams.	7.285 grams.
Ammonia driven off -----	6.972 grams.	7.490 grams.
Percent -----	98.65 %	102.60 %
Temperature of reaction --	164 degrees.	164 degrees.

<u>Formula 9.</u>	<u>No.1</u>	<u>No.2</u>
Phenol -----	200.187 grams.	200.348 grams.
Hexamethyltetramin -----	42.058 grams.	42.058 grams.
Ammonia content -----	20.428 grams.	20.428 grams.
Ammonia driven off -----	10.841 grams.	10.868 grams.
Percent -----	53.07 %	53.20 %
Temperature of reaction ---	177 degrees.	177 degrees.

Formula 10.

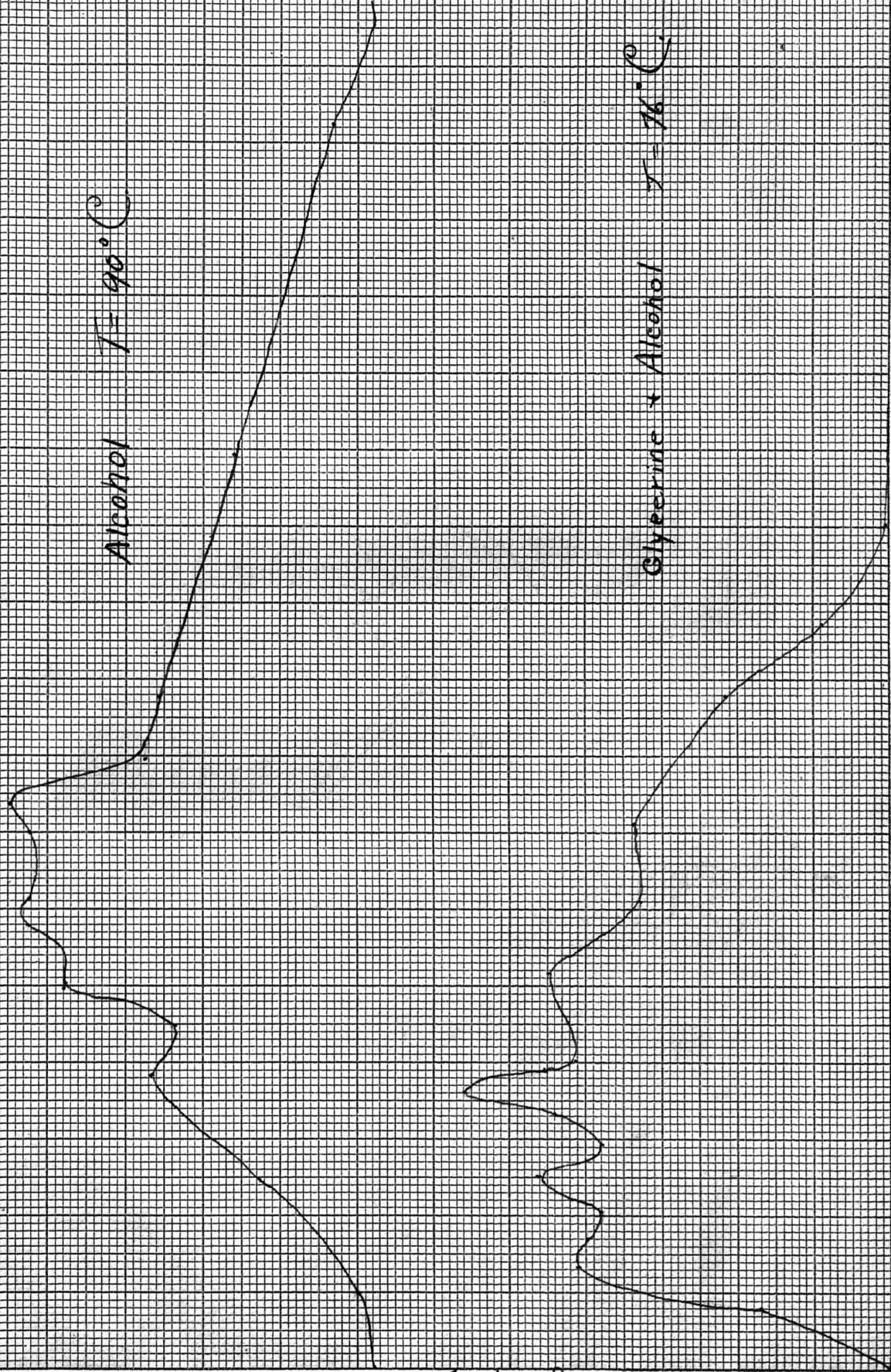
Phenol -----	80.318 grams.	80.855 grams.
Hexamethyltetramin -----	20.001 grams.	20.001 grams.
Amyl alcohol -----	300.000 c.c.	300.000 c.c.
Ammonia content -----	9.714 grams.	9.714 grams.
Ammonia driven off -----	9.501 grams.	9.403 grams.
Percent -----	97.80 %	96.80 %
Temperature of reaction ---	132 degrees.	132 degrees.

Plate. I.

Rate at which NH_3 came off

Alcohol $T = 90^\circ\text{C}$

Glycerine + Alcohol $T = 16^\circ\text{C}$



Rate ammonia per minute. \rightarrow
1 inch = 0.04 gm. NH_3

Time \rightarrow 1 inch = 1 hour

Plate II.

Rate ammonia per minute. \rightarrow
1 inch = .04 gm. NH_3

Amyl Alcohol $T = 138^\circ\text{C}$

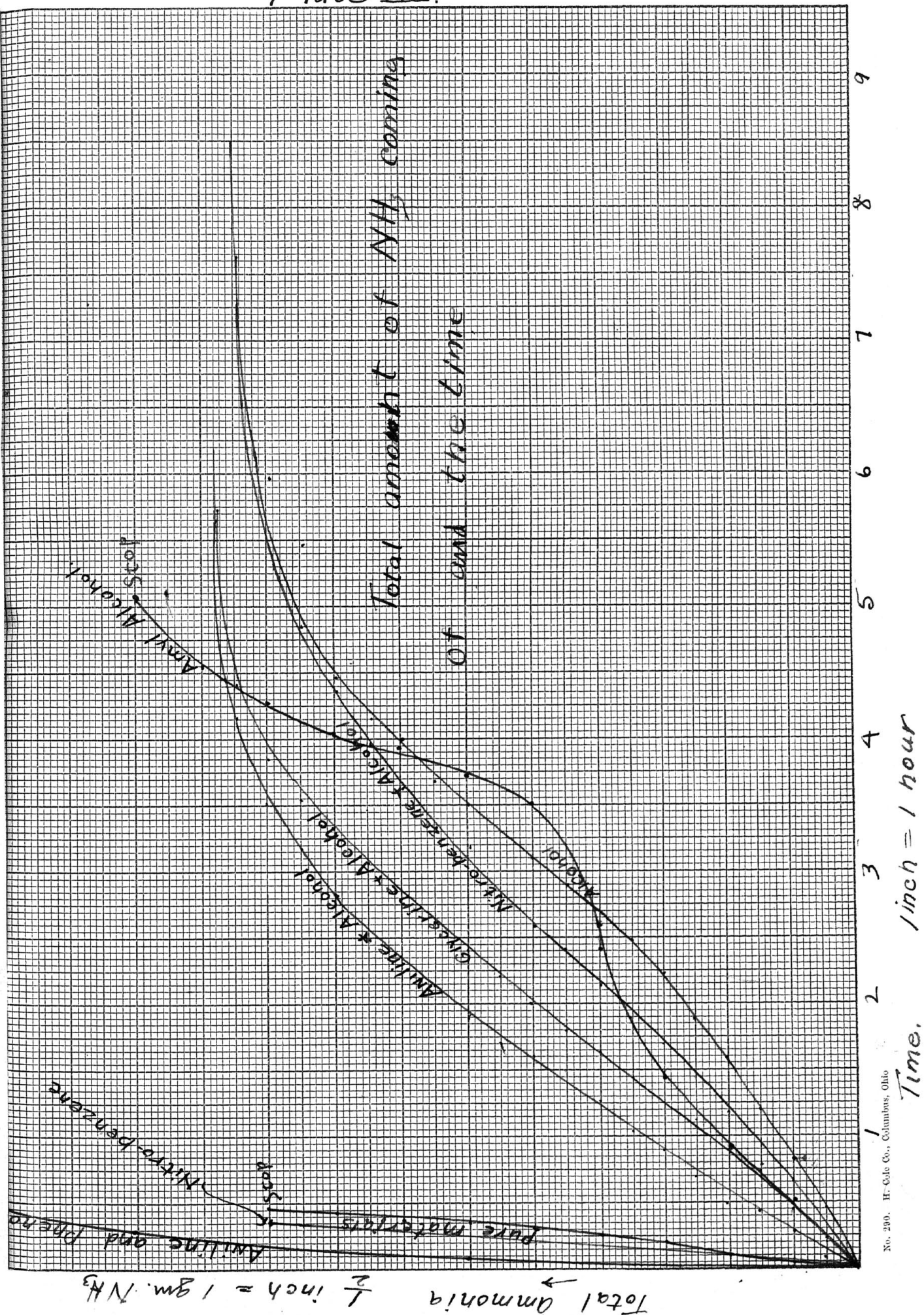
Rate at which NH_3 came off.

Aniline & Alcohol
 $T = 90^\circ\text{C}$

Nitrobenzene & Alcohol

$T = 91^\circ\text{C}$

Plate III.



PRECIPITATION OF VARNISH.

The varnish which was made with the alcohol solvent was used for the following experiments.

Alcohol was added drop by drop to a known quantity of the varnish, each drop gave a precipitate which dissolved on being shaken with the varnish. Several drops were added and the resulting precipitate was dissolved. Finally the precipitate formed by one of the drops, failed to dissolve making the solution cloudy. Every drop of alcohol from this point on gives an additional precipitate. After the addition of alcohol gave no further precipitation the precipitate formed was filtered off and washed with alcohol.

To the clear yellow transparent filtrate water was then added slowly with constant stirring. The water now gave a very flocculent precipitate, and was added from a burette until no further precipitation took place. This precipitate was also filtered and washed with water. The filtrate and washings were put in a vessel and evaporated to dryness on a water bath.

The precipitates were then dried in an oven at a temperature between 55 and 60 degrees Centigrade, they were heated until they became of a constant weight. The precipitates were very difficult to weight, they were very light and fluffy and exceedingly hygroscopic but they did not become moist or damp to feel when exposed to the air. Baekeland

also claims that his product is hygroscopic, (Jr. Ind. Eng. Chem. March 1909, page 159.) but he claims that this property is due to the potassium from the washing and which had not been entirely washed out itself latter. In this material there can be no potassium or any other substances than those put in. The large surface which the fine precipitate has seems to account for the hygroscopic property.

The substance precipitated by the alcohol was soluble in acetone. In hot alcohol it fused into a yellow ball which adhered to the side of the test tube, part of it must have dissolved for when the test tube was placed in cold water the alcohol became cloudy but after some time settled clear.

The water precipitate was soluble in alcohol, acetone, amyl alcohol, amyl acetate, aniline and nitro-benzene. Both of the two precipitates on being heated dry fuse up, then char giving a odor of burnt sugar.

ANALYSIS OF VARNISH.

Amount of varnish in grams.	Alcohol to begin pptn. in c. c.	Alcohol to end pptn. in c.c.	Alcohol washings in c.c.	Ppt. obtained in grams.	Percent of ammonia in ppt.
1. 24.214	15	200	100	2.758	7.21
2. 24.833	19	200	100	2.646	7.31
3. 2.742	2	18	25	.182	7.25
4. 4.327	2.3	18	25	.246	
5. 3.397	3.8	13	25	.188	7.51
6. 2.452	2.7	13	25	.150	
Filtrates	Water to ppt. in c.c.	Water washings in c.c.			
1.	700	500			7.676
2.	700	500			7.516
3.	150	125			.982
4.	150	125			1.220
5.	150	125			1.242
6.	150	125			.896

Note:-
The number of washings were between 10 and 15.

Weight of residues in grams.	
1.	none taken
2.	none taken
3.	.129
4.	.130
5.	.168
6.	.200

ANALYSIS OF VARNISH.

	1.	2.	3.	4.	5.	6.
Amount of varnish	24.214	24.833	2.742	3.327	3.397	2.452
Alcohol ppt.	2.758	2.646	.182	.246	.188	.150
Water ppt.	7.676	7.516	.983	1.220	1.242	.896
Residue			.129	.130	.168	.200
Totals	10.434	10.162	1.293	1.596	1.598	1.246
Amount of gum in varnish	14.280	14.630	1.632	1.963	2.004	1.448
Unaccounted for	3.846	4.630	.330	.367	.406	.202
Nitrogen content of alcohol ppts. .164		.159	*.0297		*.0210	
14 parts nitrogen require	221	219	188		210	
Average		210 parts				
Nitrogen content of water ppts. .4122		.4059	.1130		.1069	
14 parts nitrg. require.	247	245	259		266	
Average		254 parts				

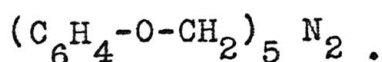
* Precipitates in 4&3 and 5&6 of the alcohol precipitation were united to find nitrogen content by kjeldahl method account of one them alone gave too small sample to work with.

CONCLUSIONS.

From the above figures a formula for the precipitates was figured although the results were far from satisfactory. In the alcohol precipitate it was found that 14 parts of nitrogen were in combination with 210 parts of oxygen and hydrogen, Assuming that the nitrogen passes off as ammonia and that the ammonia gets its hydrogen from the hydroxyl group of the phenol and the rest from the ring, an empirical formula may be worked out.

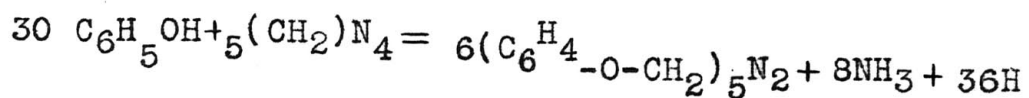
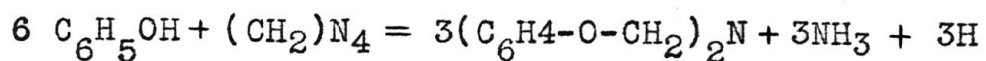
In the formula for making the varnish six moles of phenol to one mole of hexamethyltetramin were used, then one mole of phenol requires one CH_2 , formula for hexamethyltetramin being $(\text{CH}_2)_6\text{N}_4$, phenol plus the methylene radicle minus the hydrogen necessary to make the ammonia give a radicle $(\text{C}_6\text{H}_4-\text{O}-\text{CH}_2)$. This radicle has a combining weight of 106, doubling this gives 212 which is just 2 more than that which the nitrogen combines, so an empirical formula of $(\text{C}_6\text{H}_4-\text{O}-\text{CH}_2)_2\text{N}$ seems to be the correct or some multiply of this.

By the same reasoning a formula for the water precipitate was calculated. 14 parts of nitrogen required 158 parts of hydrogen and oxygen, 28 parts 316. Five times 106 is 530 very close to 516 so the formula suggested is



There is some difficulty at this point at assuming the above formulas for if we write equations for the format-

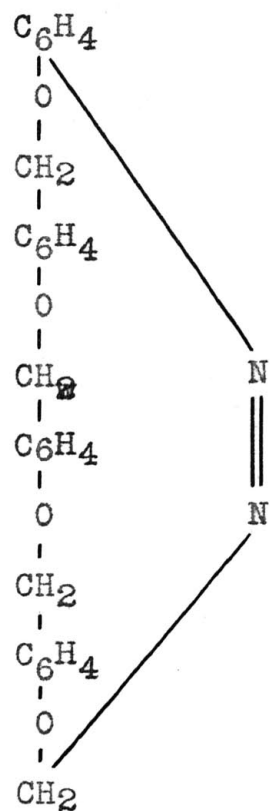
ion of the precipitates we have an excess of hydrogen in both cases unaccounted for.



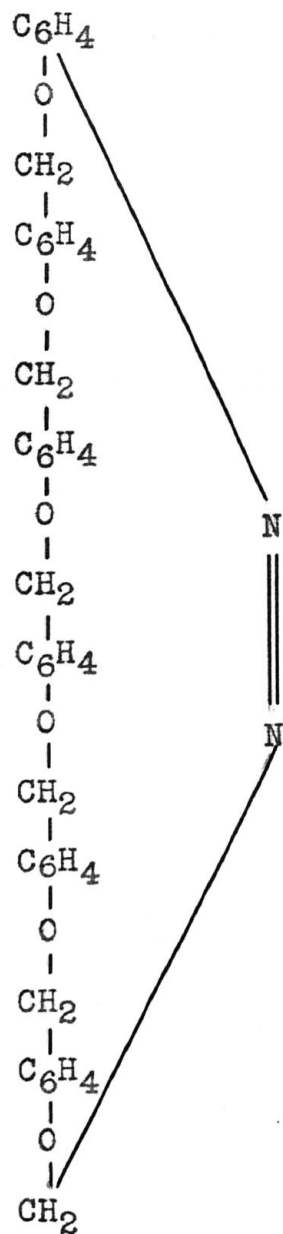
In the experiment it was assumed that all that came off was the ammonia. In the data there was a certain amount which was unaccounted for, so from this it may be judged that either the method of the experiments were at a fault or else some other volatile substance was formed and passed off without being found out. It is certain that there is no water formed so there can be no loss of oxygen. The best that can be said is to take the formulas suggested at this time until more work is carried out on the material to see if other products are formed.

Taking the formulas worked out the following structural formulas were worked out and are suggested if only ammonia passes off during the reaction.

Alcohol precipitate.



Water precipitate.



PHYISICAL PROPERTIES OF THE VARNISH.

All the varnishes dried when in a thin film to a transparent, hard, brittle varnish, having a yellowish color, sometime with a green caste. All the varnishes tended to draw under the brush, this was some what offset if aniline, nitro-benzene or glycerine were added. After drying the varnish could be heated in an open oven to a temperature as high as 250 degrees Centigrade without injury to the varnish. The varnish on heating changed gradually from a light transparent yellow to a deep red or reddish brown, the change of color depending on both the temperature and time of heating. The heating could only be done in thin films, for an increase in the thickness caused bubbling. The varnish when heated finially was insoluble in all ordinary solvents, was unattacked by cold concentrated nitric acid and concentrated sulphuric acid.

Its density is greater than that of the finger nail. The varnish has a brilliant luster as the refractive index of the artificial gum or resin is 1.645, which value is higher than any glass.

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