

recognition by your scientific colleagues and by the world of practical affairs. But in presenting you with this medal the Chicago Section of the American Chemical Society not only desires to give recognition to your discoveries in a very special way but more than that to link your name with those of the famous men who have preceded you—Arrhenius, Richards, and the one after whom the medal is named, Willard Gibbs, as well as with many more who will follow you in after years.

In the name of the Chicago Section and the founder, Mr. Converse, I now present to you the third Willard Gibbs Medal.

ADDRESS OF ACCEPTANCE

THE CHEMICAL CONSTITUTION OF RESINOUS PHENOLIC CONDENSATION PRODUCTS¹

By L. H. BAEKELAND

The preparation and utilization of some of the phenolic condensation products, of which I intend to speak, has been repeatedly described in several special publications dealing with this subject, as well as in the patent literature [see Baekeland, *THIS JOURNAL*, 1, No. 3, 149 (1909); 1, No. 8, 545 (1909); 3, No. 12, 932 (1911); 4, No. 10, 737 (1912); *Trans. Am. Electrochem. Soc.*, 15, 593 (1909); Raschig, *Z. angew. Chem.*, 25, 1945 (1912); Lebach, *Z. für angew. Chem.*, 22, 1598 (1909); Lebach, *J. Soc. Chem. Ind.*, —, — (1913)].

Many of you are acquainted with these publications. For those who are not, I shall take the liberty to state briefly that these phenolic condensation products, which have of late acquired such importance, are obtained by the action of phenol or carbolic acid on formaldehyde under suitable conditions. Instead of formaldehyde, any suitable equivalents of the latter may be used; for instance, hexamethylentetramine, which is a product resulting whenever formaldehyde and ammonia are brought together.

Whoever is not acquainted with organic chemical reactions may be somewhat astonished to learn that two very ill-smelling liquids, like carbolic acid and formaldehyde, should be capable, by an act of chemical synthesis, to engender an absolutely different substance which is solid, hard and infusible, insoluble in all known solvents, resists most chemicals, and which from its external appearance might be mistaken for the most beautiful amber, or for the highest quality of Chinese or Japanese lacquer. If it differs at all from any of the latter products of nature, it is mainly by its superior strength and higher resistive qualities, and by its incomparably lower cost of production.

To those of you also who are still unfamiliar with this substance, it may help your imagination, when it comes to conceive the possible uses thereof, to examine the rather varied exhibit displayed here to-night, of the many articles which have been made by means of these infusible phenolic condensation products. You will notice that these applications vary from cigar holders to switchboards for battleships; from grindstones to self-lubricating bearings; from the most effeminate jewelry, to acid pump valves; from brass-bedstead lacquer, to phonograph records; from billiard balls to automobile magnetos; from unbreakable dolls, to electrical machinery; from buttons to newspaper stereotyping matrices.

I may add that since I made my first publication on this subject, a number of important and prosperous new industries have been brought into life, and an ever-increasing number of new applications are looming up as fast as the technique of this material is being mastered by a larger number of skilled men.

To get as far as we are now, has been by no means easy work, and even now, much had to be left undone or half finished. Only those who ever have undertaken pioneer work can conceive what all this involves, especially when a subject of such a wide range of applications has to be handled, and when those skilled in the art are few and have first to be patiently trained.

In my eagerness to go ahead, progress seemed rather too

slow to me at first, but now that I am beginning to see everywhere the practical results in many different directions, I am reminded of the fact that, after all, it is only a short time ago that the systematic commercial manufacture of the raw products was started. Since then, several factories here and abroad are supplying the raw material in many grades to the numerous industries which have learned to utilize it for the most varied purposes.

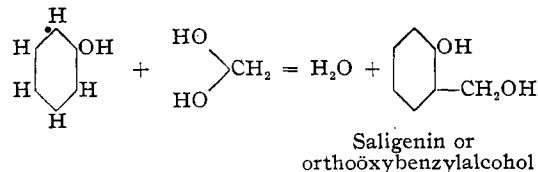
In the meantime, dozens of highly trained chemists and engineers, in Europe as well as here, are spending their daily efforts in the study of further improvements in this new branch of chemical industry, and on the applications dependent thereon. Up till now this country has kept the lead in this industry, although in some European countries, too, much good work has been performed.

While the practical work has been going on steadily, the problem of the purely theoretical side has not been neglected; I now want to devote this opportunity to present this part of the subject. Unfortunately, the study of the chemical reactions involved in these processes is certainly not an easy one. Any organic chemist knows that bodies of a resinous or colloidal nature, which neither crystallize, nor melt, nor distill, nor dissolve, do not belong to the class of substances easy to purify nor to be studied with some hope of accuracy, approaching even in the most remote way what can be accomplished with clearly crystalline or volatile substances.

Neither will chemists be very astonished if such men like Adolf von Bayer, or his pupils, when as far back as 1872 (*Ber.*, 5, 25, 280, 1094, 1095; 19, 3004, 3009; 25, 3477; 27, 2411) they took up the study of condensation products of aldehydes with phenols, were not much attracted by some of the resinous substances which now and then were formed in these reactions, and preferred to devote their attention to the crystalline, well-defined bodies which could be studied with incomparably surer and easier methods.

The same happened with Kleeberg, who in 1891 (*Ann.*, 263, 283), in further work on condensation products, encountered a hard, untreatable substance of which the further study was abandoned in favor of some crystalline condensation products.

I should remind you of the fact that by conducting the action of formaldehyde on phenol under suitable conditions [Lederer, *J. prakt. Chem.*, [2] 50, 224; Manasse, *Ber.*, 1894, 2409-2411; U. S. Pat., Manasse, 526,786, 1894; D. R. P., Bayer, 85,588] a very clean-cut reaction takes place, giving the simplest phenolic condensation product, oxybenzylalcohol or saligenin. In this case, formaldehyde reacts as methylenglycol:



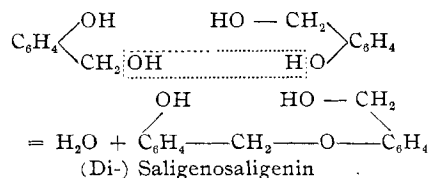
In this same reaction, more or less large amounts of para-oxybenzylalcohol are formed at the same time. But saligenin or oxybenzylalcohol is very easily disturbed by dehydration, and then changes into a resinous mass. This dehydration can occur by simple application of heat, and is much hastened by the presence of strong acids or other chemical agents. This is the reason why in the processes of the preparation of oxybenzylalcohol, low temperatures and general careful treatment are essential. For this purpose, the phenol is first changed to phenolate by the introduction of one molecule of alkali hydrate; the reaction is carried out at moderate temperatures, and afterwards, the oxybenzylalcohol is set free by the judicious addition of weak acids and by extraction by means of fractional solvents.

Unless such careful precautions be observed, the reaction gets

beyond control, and resinous bodies are sure to be produced in predominant quantity. This is especially the case when strong acids are used as condensing agents; but even under such conditions we have succeeded, in my laboratory, in establishing the presence of noticeable quantities of oxybenzylalcohol [Backland, *THIS JOURNAL*, 4, No. 10 (1912)]. However, continued application of heat, or the presence of strong acids, or other condensing agents, will soon cause resinification of any of the above-mentioned phenol alcohols, so that in the process of preparation of phenol alcohols, the conditions of procedure and necessary precautions are widely different from those required in the production of synthetic resins.

The resinous dehydration products, derived from phenol alcohols, are known and have been described long ago as saliretin products [Beilstein, *Org. Chem.*, 2, 1109 (1896); R. Piria, *Ann. Chem.*, 48, 75; 56, 37; 81, 245; 96, 357; Moitessier, *Jahresbericht*, 1886, 676; K. Kraut, *Ann. Chem.*, 156, 123; Gerhardt, *Ann. chim. phys.*, [3] 7, 215; F. Beilstein and F. Seelheim, *Ann. Chem.*, 117, 83; C. Schotten, *Ber.*, 1878, 784].

Some have proposed a chemical structural formula for these products. For instance, it has been assumed that the first dehydration product disaligenosaligenin is formed as follows:



In the same way, a trisaligenosaligenin, $\text{C}_{28}\text{H}_{26}\text{O}_5$ or $4\text{C}_7\text{H}_8\text{O}_2 \cdot 3\text{H}_2\text{O}$ (K. Kraut, *loc. cit.*; Gerhart, *loc. cit.*), and a heptasaligenosaligenin, $\text{C}_{36}\text{H}_{30}\text{O}_9$ or $8\text{C}_7\text{H}_8\text{O}_2 \cdot 7\text{H}_2\text{O}$ (F. Beilstein and Seelheim, *loc. cit.*), are formed.

However attractive all such formulae may appear to enthusiastic novices in organic chemistry, the sobering fact remains that every one of above-mentioned substances is of a highly resinous nature. Their very name, "saliretin," has a Greek root which refers to their resinous properties. Whether their constitution is as simple as is indicated by the above formula, is a mere matter of conjecture and entirely impossible to prove by any of the scientific methods available at present. Quite to the contrary, it is more probable that these substances not only have a considerably more complicated molecular structure, but that they are mixtures of several colloidal bodies which exist here together in solid solution. Furthermore, the phenomenon of dehydration may be accompanied by rearrangement of the molecules (Umlagerung). All that we can state with any degree of certainty is that oxybenzylalcohol, by a process of dehydration, loses water and turns into ill-defined resinous bodies designated under the generic name of saliretins. To try to establish nearer the structural constitution of their molecules is out of the question. That the gradual elimination of water should decrease the fusibility of these bodies and accentuate their insolubility, seems almost self-evident to any chemist and requires no further explanation.

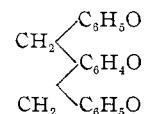
DeLaire was the first, by his published patents (DeLaire, D. R. P., 189,262; British Patent, 15,517, 1905; French Patent, 350,180) to demonstrate the obvious relation of the so-called fusible condensation products with phenol alcohols and saliretin resins, by showing that these phenol alcohols can be transformed industrially by dehydration into fusible resins or saliretin products suitable for commercial purposes, in place of shellac, copal or other natural resins. He showed, furthermore, that in this process, it is not necessary to first produce the phenol alcohol in pure form, but that the two succeeding reactions (condensation and further dehydration with formation of saliretin resins) can be carried out practically at the same time, so that the phenol alcohol is dehydrated to saliretin as soon as it forms.

As stated above, direct experiments in my laboratory have conclusively shown that even when hydrochloric acid is used as condensing agent, in presence of phenol and formaldehyde, notable amounts of phenol alcohol are formed at first, which soon undergo complete resinification by further application of heat.

These fusible resins, or saliretin products, are practically identical with those described by Blumer a few years earlier (Louis Blumer, British Pat., 12,880, 1902). However, the relationship of these fusible resins might escape notice by the fact that these resins are generally more fusible and soluble than pure saliretin; furthermore, these artificial resins do not, on further application of moderate heat, lose their fusibility, unless under special conditions. But these differences are merely due to the fact that the commercial resins of the Blumer or DeLaire fusible type always contain more or less free phenol or cresol, which forms a solid solution and confers upon them higher and more permanent fusibility. I have already published the fact that if this excess of phenol is removed by suitable means, the fusibility and solubility of these substances is soon impaired (Eighth International Congress of Chemistry, New York, September, 1912; *THIS JOURNAL*, 4, No. 10) and the fusible resin behaves then generally as the pure saliretin resulting from the dehydration of pure phenol alcohol.

The above-mentioned facts, easy to follow, give us a rather simple practical interpretation as to the chemical parentage of the so-called fusible, soluble phenol-formaldehyde resins, so that we can consider them as saliretin products, or so-called dehydration products of the corresponding phenol alcohols. However, this is about as far as we can go. As soon as we try to propose any theory about their molecular structure, we leave the terra firma of established facts, and we enter the nebulous realm of gratuitous assumptions and hypothesis.

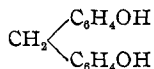
Mr. J. W. Aylsworth (U. S. P., Aylsworth, 1,020,593) forms the fusible soluble resin by direct action of three molecules of phenol on two molecules of formaldehyde, without condensing agents. He calls this substance "phenol resin," and assumes its constitution to be



In discussing the latter formula, Dr. H. Lebach (*Soc. Chem. Ind.*, 1913) calls attention to the fact that, outside of the relative proportions in which the ingredients are used, we have no other justification for this formula. Dr. Lebach, furthermore, brings out the fact that in the material obtained after Aylsworth's description, decided amounts of free phenol are known to exist. Mr. Aylsworth's interpretation of the constitution of these fusible resins, may be nearer or farther from the truth than the structure formula proposed by others for these saliretin bodies. Or what is more probable, all these fusible resinous substances may be composed of two or several individual chemical bodies all mixed in varying proportions and forming a colloidal solid solution with each other. This applies to any of these resins, whether they are obtained by direct action of phenol on formaldehyde, or whether they are made step by step by the intermediary formation of phenol alcohol and subsequent dehydration thereof. Some of these substances may or may not be simple dehydration products of phenol alcohols derived therefrom by simple union of several molecules with elimination of water, after the same reaction by which ether or ethyl oxide is formed by the elimination of water between two molecules of alcohol. Or again, the process of dehydration may possibly be complicated by more far-reaching transformations, transpositions, or rearrangements of the molecule.

That diphenylmethan compounds seem to play some rôle in

this reaction is proved by the fact that we have succeeded in isolating from the initial mass of phenol, formaldehyde and hydrochloric acid, appreciable amounts of paradioxydiphenylmethan,



alongside of the oxybenzylalcohols mentioned above. Whether paradioxydiphenylmethan is formed here directly or whether it is the result of the action of initially formed phenol alcohol on a further molecule of phenol, are questions of minor importance in a matter-of-fact interpretation of these complicated reactions.

At any rate, the formation of bodies of the diphenylmethan group seems to be one of the probable accompaniments of that peculiar resinification process, whereby phenol alcohols are transformed by dehydration, into saliretins, or whereby phenol and formaldehyde are directly condensed to the same kind of fusible resins.

Dr. F. Raschig has properly called our attention to the fact [Raschig, *Z. angew. Chem.*, **25**, 1945 (1912)] that in case diphenylmethan derivatives are formed, a large number of isomers can exist and a variety of reactions can take place at the same time, or may succeed each other. He, too, brings out the opinion that it becomes utterly impossible, even with all the means which science has put hitherto at our disposal, to separate and identify these different bodies. We might attempt to do so with products which can be isolated by fractional crystallization, precipitation, or fractional distillation. But with amorphous colloidal bodies, intermixed with each other in solid solution, this becomes a hopelessly impossible task.

Dr. Raschig expressed the opinion that the soluble resin in reality is a mixture of the three isomeric dioxydiphenylmethans, rendered impure by an excess of free phenol, and some of the phenol alcohol corresponding to dioxydiphenylmethans. Unfortunately, this simple interpretation is not substantiated by the fact that the soluble resin, treated with boiling water, does not give off serious amounts of dioxydiphenylmethan, although the latter is very soluble in boiling water, and should, therefore, be readily separated by this method. Even by very careful treatment, merely small amounts of these crystalline bodies can be separated.

Nevertheless, all these fusible, soluble phenolformaldehyde resins described by Blumer, DeLaire, Lebach (Knoll-Wetter), Bayer & Co., Aylsworth, and others, have practically the same chemical and physical properties, differing only in minor details by the way in which they are prepared and by the more or less large amount of free phenol they may contain [Baekeland, *THIS JOURNAL*, **1**, No. 3, March, 1909; **1**, No. 8, Aug., 1909; **4**, No. 10, Oct., 1912; DeLaire (*loc. cit.*), as well as myself, has also shown how these very same fusible resins are obtainable in pure state by direct dehydration of phenol alcohols, which identifies them practically as saliretin bodies. At the same time, I have been able to point out the great importance of the presence of small quantities of free phenols which tend to insure their fusibility and solubility. Furthermore, I have been able to produce these same fusible and soluble resins by simply heating phenol alcohol or saliretin in presence of some free phenol [Baekeland, *THIS JOURNAL*, **1**, No. 8 (1909)].

On the other hand, we have succeeded also in producing a fusible phenol resin by heating for 3 hours at 180° C., 100 grams of paradioxydiphenylmethan with 10 grams of paraform in a sealed tube.¹

By increasing the proportion of paraform, we have succeeded by the same method, in producing a very hard and infusible amorphous colloidal body, of very high resistivity to most chemicals and solvents.

This fact seems to indicate that diphenylmethanphenols

¹ This proportion would correspond approximately to 15 molecules of phenol reacting on 14 molecules of formaldehyde.

may, indeed, be used as a starting point, or may be formed among the transition products, in the formation of the so-called fusible, soluble condensation products, as well as the infusible, insoluble condensation products.

There is, nevertheless, another fact which proclaims eloquently the saliretin-like nature of these fusible phenolic resinous condensation products. The latter can be obtained by reduction of salicylic acid [Baekeland, *THIS JOURNAL*, **4**, No. 10, Oct., 1912; Velden, *J. prakt. Chem.*, [2] **15**, 164; *Jahresbericht*, 1877, 337].

For the sake of clearness, before leaving the subject of these relatively simple fusible soluble phenolic condensation products, I should mention that I have proposed, heretofore, to designate them all under the generic name of Novolak: this merely as a means for grouping under the same denomination, products of the same composition and properties, although they have been prepared by different methods and described by several other investigators, like Blumer, DeLaire, Lebach and Aylsworth, etc. I believe we can just as well call them fusible saliretin products.

From different sources many attempts have been made as far back as 1902, to utilize these soluble artificial resins, as shellac substitutes, or as substitutes for other natural resins in the manufacture of varnish. In this respect, they were of special interest, a few years ago, when the market price of shellac was unusually high. As far as my own experience goes, and as far as I have been able to ascertain from others, none of these products have fulfilled the expectations of industrial use.

Nowadays, the main importance of these shellac substitutes (Novolak or saliretin resins) resides in the fact that they bear an immediate relationship to another class of bodies, the so-called infusible insoluble phenolic condensation products, which have been designated by such names as bakelite, resinit, condensite, and which Dr. Lebach called "resites."

We shall now try to discuss the chemical constitution of these infusible condensation products of maximum hardness and resistivity.

The very fact that the latter-mentioned bodies are infusible and insoluble, and that they are characterized, furthermore, by a much more pronounced chemical and physical inertness than the so-called Novolak resins or saliretin products, emphasizes still more the unusual difficulty which confronts us in the study of the chemical constitution of these bodies. If it is practically impossible to indicate with any degree of certainty the molecular constitution of the relatively simple saliretin bodies, our task becomes incomparably more difficult here.

Moreover, we should take into consideration that in the industry, these products are made from commercial carbolic acid, containing besides phenol, variable amounts of ortho-, meta-, and para-cresol, and other homologs and isomers. We should also bear in mind that each of these homologs may act differently and not only may produce isomeric bodies, but these isomeric bodies may react one upon another in decidedly different ways, and thus greatly influence the progress of the reaction as well as the physical and chemical properties of the final products.

Under the circumstances, it becomes simply impossible to try to characterize by a general scientific interpretation either the reaction which engenders those bodies, or the molecular constitution thereof. All that we can say, with some degree of probability and without embarking wildly on fantastic hypotheses, can easily be summed up as follows:

First: That these bodies are phenolic condensation products of formaldehyde, or of equivalent methylene-group-containing substances, this condensation process having for result, a corresponding enlargement of the so-called carbon nucleus of the molecule.

Furthermore, it is a well accepted fact that in these reactions,

by them, becomes so limitlessly large that we know of no scientific methods which would enable us to identify them all. Commenting on this fact, he states that the amorphous character, as well as the valuable technical qualities of the end products, are probably due to the great variety of the different bodies which are all contained therein, including at the same time, extraneous bodies like free phenol, etc.

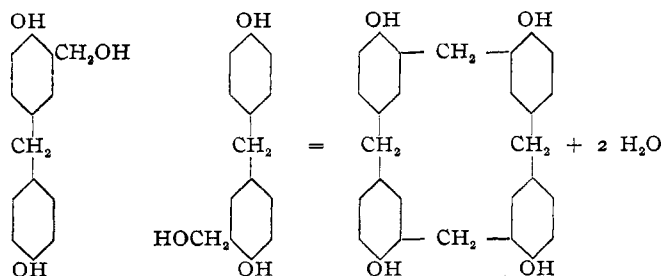
Dr. Raschig seems to infer, however, that the production of the soluble variety resinous condensation products is merely determined by the relative amounts of phenol and formaldehyde. He says: "Der Unterschied zwischen den löslichen Harzersatzmitteln und dem unlöslichen Bakelit besteht nun im wesentlichen darin, dass man bei Herstellung der ersteren auf 1 Mol. Phenol weniger als 1 Mol. Formaldehyd, in der Regel nur 0,5 Mol., beim letzteren aber mindestens 1 Mol. Formaldehyd, in der Regel 10-20% mehr zur Anwendung bringt." And he goes on to state that in case insufficient formaldehyde be used, a mixture of the three isomeric dioxydiphenylmethans should be the result, while if more formaldehyde is present, then the corresponding phenol alcohols of those dioxydiphenylmethans will be formed; the latter can react further upon another, and in this way build up a much larger molecule which accounts for the insolubility and great resistivity of these large molecules, of which the dynamics are correspondingly decreased.

I take the liberty of pointing out that this theoretical interpretation holds good only to a certain extent. If it is possible, and even probable, that some of the bodies mentioned by Dr. Raschig exist in the first phases of the reaction, or may exist in the final products together with an endless variety of other chemical individuals, we know next to nothing of the relative importance thereof, whether they exist as traces, or whether they play a fundamental rôle.

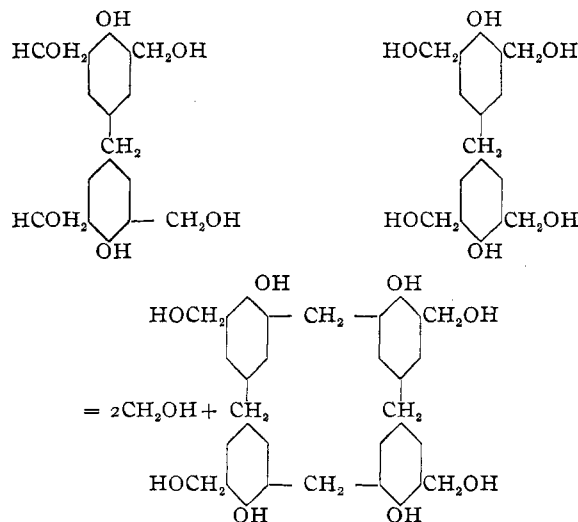
Furthermore, in his generalizations, in relation to the influence of relative quantities of phenol and formaldehyde, Dr. Raschig seems to overlook the very important and well established fact that the nature of the condensing agent has an enormous influence on whether fusible or infusible products will be formed. For instance, it is known that if you operate in presence of small amounts of bases, infusible condensation products will be the result, whether you use an excess of phenol or not [Baekeland, *THIS JOURNAL*, 1, No. 8, (1909); 4, No. 10 (1912)].

In addition to the foregoing, we should not lose sight of the possibility that in all these rapidly succeeding reactions, we may have several cases of rearrangement or transposition of the molecule (Umlagerung).

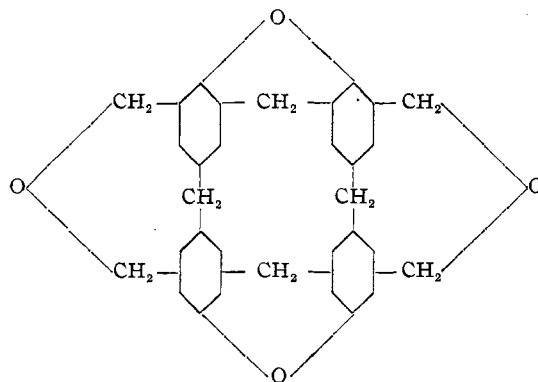
Dr. Raschig has outlined some further theoretical interpretations from the standpoint of the assumption that diphenylmethan derivatives are the main products in this process. He has shown, for instance, how under certain conditions a body may be conceived which he calls Bakelite I



and then again another body resulting from a larger proportion of formaldehyde,



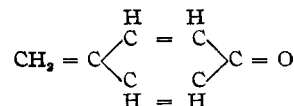
which after dehydration gives a molecule which Raschig calls Bakelite II:



Much as these speculative considerations, presented by a scientist of reputation, may be able to give us food for thought, we must not forget that one hypothesis is about as easy to propose as another as long as we are unable to use any of the methods for determining molecular size and molecular constitution.

Even Dr. Raschig warns us, with the natural conservatism of an able chemist of long and wide experience, when he says: "Ueber die Chemie des Bakelits tappen wir noch vollständig im Dunkeln."

Of late, Wohl (*Berichte*, 45, 2046) has advanced a radically new hypothesis which considers these bodies as polymerization products of methylene derivatives of the tautomeric phenol,



and he advanced this opinion after the study of acrolein derivatives of phenols and of the so-called resorcin ethers.

Before leaving this subject, I should mention that we have tried to verify the statement of Dr. Raschig that orthoöxybenzylalcohol, treated alone with a condensing agent, does not furnish bakelite, and that paraoxybenzylalcohol acts in the same way while bakelite is produced with its characteristic insolubility from the mixture of both. He deduced from this that both para- and orthocompounds are needed for the production of bakelite. In a footnote, however, he mentions that both ortho- and paraoxybenzylalcohol, after long heating, furnish bakelite of typical insolubility in alkali; but that the reason for this is to be found in the fact that both phenol alcohols split by and by

in formaldehyde and phenol which then can unite again and form the other phenol alcohol, so that finally a mixture is formed of ortho- and paraoxybenzylalcohol.

The paraoxybenzylalcohol used in our own experiments was mostly prepared by Auwers' method and had a melting point of 110° C. to 112° C. Auwers and Daecke (*Ber.*, 32, 3374) indicate 124.5° C.-125.5° C. as the melting point of paraoxybenzylalcohol, while Manasse (*Ber.*, 27, 2411) and Lederer (*J. prakt. Chem.*, [2] 50, 225) indicate 110° C.

We found that when orthooxybenzylalcohol (saligenin) or paraoxybenzylalcohol, or a mixture of equal parts of both together with a small amount either of ammonia or of caustic soda is heated in a sealed tube to 160° C. for about 6 hours, products are obtained which are practically the same and which are identical in their properties with the so-called polymerized saliretins. Indeed, they are all considerably inferior in chemical resistivity to bakelite of highest hardness and resistivity. They soften on heating, but are infusible, are much more brittle than the hardest obtainable products of the kind, and begin to break up immediately, without dissolving, when treated with acetone or with 20 per cent caustic soda.

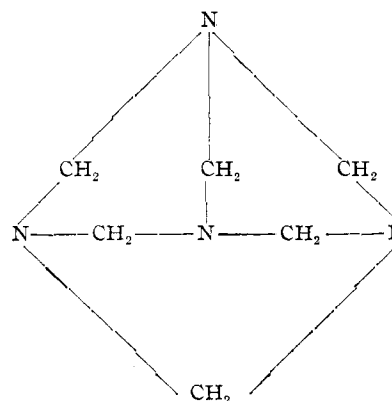
On the other hand, when paraoxybenzylalcohol is mixed with 5 per cent paraform (this corresponds about to the proportions of 6 mols. phenol to 7¹/₄ mols. formaldehyde) and heated in a sealed tube, decidedly different products are obtained which not only are infusible, but do not soften by application of heat, and are as hard as the hardest and most resistive bakelite, and are not attacked by acetone or by 20 per cent caustic soda.

It seems, therefore, that the products obtained by Dr. Raschig belong to that variety which I described as polymerized saliretins, and which do not possess, by any means, the maximum hardness nor chemical resistivity of the products which are formed whenever there is sufficient formaldehyde or equivalents thereof present [Baekeland, *THIS JOURNAL*, 4, No. 10 (1912)].

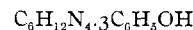
In whatever theoretical speculations we engage on this subject, we must not lose sight of the fact that the nature of the condensing agent may have an enormous influence on the way the reaction takes place, even if at the end the products may look very much alike and be more or less identical.

For instance, when an acid condensing agent is used, the process seems to proceed very differently from what happens when alkalis are used (Baekeland, *loc. cit.*). Then again, when ammonia is used, the reactions which succeed each other seem to be quite different. In the latter case, they can be followed to quite an extent [Lebach, *Z. angew. Chem.*, 22, 1601 (1909)].

For instance, every chemist knows that ammonia on acting on formaldehyde produces immediately hexamethylentetramine:



In the same way, if ammonia be added to a mixture of phenol and formaldehyde, the same hexamethylentetramine is formed independently whether the phenol or the ammonia be added first or last. In presence of the phenol, one molecule of hexamethylentetramine adds to three molecules of phenol and gives



hexamethylentetramintriphenol (Tollens and Moschatos, *Liebigs Ann.*, 272, 280; Wohl, *Ber.*, 19, 1892; Tollens, *Berichte*, 17, 643; Carl Goldsmith, *Verlage von Friedrich Cohn*, 1903, 29; Cambier, *Brochet Compl. rend.*, 120, 557; Lebach, *Z. für angew. Chem.*, 1909, 1600; Beilstein, *Handb. der Organ. Chem.*, 2, 37, 651).

Under the action of heat, this latter substance decomposes and sets free large amounts of ammonia gas, leaving finally a hard, infusible body. But the ammonia can act immediately on new amounts of formaldehyde, and repeat the same reaction so that a small amount of ammonia is sufficient to act as catalytic agent for all the formaldehyde present, and to carry on the whole reaction to the finish, after which free ammonia is found in the product.

The general reaction seems to be the same whether ammonia and formaldehyde be used in conjunction with phenol, or whether phenol be made to react directly on hexamethylentetramine or whether hexamethylentetramintriphenol be decomposed by heat. In the latter case, however, the final product is very porous and does not present a colloidal mass sufficiently homogeneous for technical purposes. On this account the use of a somewhat larger amount of phenol or other suitable similar body becomes imperative, so as to obviate this defect. Hence, some excess of phenol, or suitable solid solvent, will accomplish technical results which are not otherwise possible when hexamethylentetramine is used alone.

YONKERS, N. Y.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

THE ELECTROCHEMICAL INDUSTRIES OF ITALY

The last report of the "Societa Italiana d'Elettrochimica" contains an account of the status of the electrochemical works and of the developments during 1912.

The second Pescara waterfall was brought into work during 1912, and electric power, at a voltage of 80,000 to 88,000, was conveyed to Naples at the close of the year. The production of sodium hydroxide at the Bussi Works amounted to 3,500 metric tons. The production at the commencement in 1905-1906 was only 1,820 tons; but it now seems that the limit of the capacity of the plant has been reached. Attention is being directed to the manufacture of chlorinated products, for which the works is utilizing all the chlorine, but a regular market has not so far been found. There was a considerable increase in the

production of hydrochloric acid, for which there are many markets in Italy, and carbon tetrachloride was exported. Notwithstanding these developments, the profits of the works were somewhat less than those of the previous year, namely, 336,498 instead of 350,877 lire; this is attributed to the high cost of fuel, and electric boilers are now about to be installed with a view to economy.

THE MATCH INDUSTRY OF SWEDEN

It has been announced that ten of the twelve independent match factories in Sweden, which have remained outside the so-called Swedish match trust, are to be formed into a single corporation to be known as "Aktiebolaget Förenade Svenska Tändsticksfabriker." The annual output is to be 8,000,000