

Any one wishing all four would pay \$3 additional. If we assume that 500 would do this (a liberal estimate) this would give \$1500, while about \$2800 would be saved by the decrease of 3500 copies in the total circulation of the three journals. Such a plan would, in effect, add \$3 to the dues of all who wished, as now, to have access to original papers in all fields and would deprive all the rest of the papers in some one field. The increase would be especially felt by students and young men just beginning their professional career. The injury which would result from giving to the majority of our members a one-sided literature appears to me very serious. We ought not to think chiefly of the members of the council of the society and of chemists of similar character and position but rather of members with limited means and of the many who are isolated so that the journals published by the society are the only ones they can see. The decreased circulation would also make the journals less attractive as a means of publication and might also interfere seriously with advertisements.

(3) An increase of \$1 in the dues would somewhat more than meet the increased expense. It seems to be generally agreed that such a plan is wholly inadvisable and that the dues must not be increased again for any purpose.

(4) Add 640 new members. Even with the four journals it would cost only about \$5 to print an extra copy of each, pay the postage, and pay the additional expenses for the secretary, local sections, etc. Hence each new member adds \$5 to the funds available for publication.

(5) Secure an endowment for publication. Every one will admit, I think, that the maintenance of our publications is of very great importance for the future of chemistry in America and it does not seem too much to hope that some of the leaders of industries which have profited so largely by our science may yet contribute liberally to their support. What has been accomplished during the past two years is certainly a sufficient basis for an earnest appeal.

It seems to be clear from what has been said that we ought to wait for the publication of a journal of physical chemistry till it is possible, financially, to do this and send the journal to all of our members. For the first time in the history of chemistry the American Chemical Society has succeeded in uniting all classes of chemists in a large organization which cares adequately for the interests of

both pure and applied science. Those of us who attend the general meetings of the society see very clearly the advantages which come from the association and acquaintance of chemists with radically different habits of work and points of view. But we must remember that, after all, these meetings reach only a small fraction of our membership, while the journals now go to all of our members. We have recently provided, by the establishment of this Journal, a more suitable form of publication for articles in industrial and engineering chemistry. I am sure that industrial chemists would be the last to say that we ought not to continue to provide, as in the past, for the suitable publication of researches which have been undertaken without reference to any industrial application.

W. A. NOYES.

#### SAMPLING.

MR. BAILEY has done a service to analytical chemistry by his careful physical and mathematical investigation of sampling, the results of which are published in this number. While the work concerns itself with the sampling of coal, the results are of wide application. In the past, and at the present time, in thousands of cases the analysis has to bear the criticism which should fall upon improper sampling. The analyst, who is not his own sampler, can analyze only the sample which is delivered to him. Almost any analyst can relate how samples representing carload lots of coal were delivered to him in pint milk bottles and lubricating greases in candy sacks. Members of the engineering profession are not altogether blameless in encouraging faulty sampling, and occasionally the chemist himself is deserving of censure in this regard. The simple truth that a correct analysis is dependent upon a correct sample, would appear to be sufficiently axiomatic to require no demonstration.

W. D. RICHARDSON.

## ORIGINAL PAPERS.

### THE SYNTHESIS, CONSTITUTION, AND USES OF BAKELITE.<sup>1</sup>

BY L. H. BAEKELAND, SC.D.

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Since many years it is known that formaldehyde may react upon phenolic bodies. That this re-

<sup>1</sup> Read before the N. Y. Section of the American Chemical Society on February 5, 1909.

action is not so very simple is shown by the fact, that according to conditions of operating or to modified quantities of reacting materials, very different results may be obtained; so that bodies very unlike in chemical and physical properties may be produced by starting from the same raw materials. Some of these so-called condensation products are soluble in water, other ones are crystalline, while some others are amorphous and resin-like. Then again, among the latter resinous products some are easily fusible and soluble in alcohol or similar solvents while other ones are totally insoluble in all solvents and infusible. This paper will deal with a product of the latter class.

The complexity of my subject compels me to make a brief historical outline which will allow us to form a clearer idea of the scope of my work and differentiate it from prior or contemporary attempts in subjects somewhat similar.

That phenols and aldehydes react upon each other was shown as far back as 1872 by Ad. Bayer and others.<sup>1</sup>

The substances obtained by these investigators were merely of theoretical interests and no attempt was made to utilize them commercially; furthermore their method of preparation was too expensive and too uncertain and the properties of some of their resinous products were too undecided to suggest the possibility of utilizing them for technical purposes.

Until 1891 attempts at synthesis with formaldehyde were generally limited to the use of its chemical representatives, either methylal, methylen acetate, or methylen-haloid-compounds.

With the advent of cheap commercial formaldehyde, Kleeberg<sup>2</sup> took up again this subject using formaldehyde solution in conjunction with phenol and in presence of strong HCl. Under spontaneous heating he obtained a sticky paste which soon becomes a hard irregular mass. The latter is infusible and insoluble in all solvents and resists most chemical agents; boiling with alkalis, acids or solvents will merely extract small amounts of apparent impurities.

As Kleeberg could not crystallize this mass, nor purify it to constant composition, nor in fact do anything with it after it was once produced, he described his product in a few lines, dismissed the subject and made himself happy with the study of nicely crystalline substances as are obtained by the

action of formaldehyde and polyphenols, gallic acid, etc.

The mass obtained after Kleeberg's method, is a hard and irregular porous substance containing free acid which can only be removed with difficulty after grinding and boiling with water or alkaline solutions. The porosity of the mass is due, as we shall see later, to the evolution of gaseous products during the process of heating.

In 1899 Smith,<sup>1</sup> realizing probably that Kleeberg's method does not lend itself to molding homogeneous articles, tried to moderate the violent reaction by using a solvent like methyl-alcohol or amyl-alcohol in which he dissolves the reacting bodies, as well as the condensing agent, muriatic acid. Even then the reaction is too violent if formaldehyde be used, so he does not use formaldehyde, but instead he takes expensive acetaldehyde and paraldehyde, or expensive polymers of formaldehyde. After the reaction, he slowly evaporates the mixtures and drives off the solvent at 100° C. He thus obtains, by and by, a hardened mass in sheets or slabs which can be sawed, cut or polished. In his German patent specification<sup>2</sup> he insists on the fact that in his process the methyl- or amyl-alcohol not only act as solvents but participate in the reaction and he states that this is clearly shown by the color of the final product, which is dependent on the nature of the solvent he employs. He mentions that his drying requires from 12-30 hours; my own experience is that it takes several days to expel enough of the solvent; and even after several months, there is still a very decided smell of slowly liberated solvent. During the act of drying I observed in every instance warping and irregular shrinking of the mass which thereby becomes deformed and makes this method unfit for accurate molding.

In 1902 Luft,<sup>3</sup> tried to overcome these difficulties in a somewhat similar way. Like Kleeberg he uses a mixture of formaldehyde, phenol and an acid; but recognizing the imperfections of the product and desiring to make of it a plastic that can be molded, he mixes the mass before hardening, with suitable solvents such as glycerine, alcohol or camphor. He virtually does the same thing as Smith with the difference, however, that he adds his solvents *after* the main reaction is partially over and uses his acid condensing agent in aqueous solution. His aim, as clearly expressed in his

<sup>1</sup> *Ber.*, 5, 1095; 19, 3004 and 3009; 25, 3477; 27, 2411.

<sup>2</sup> *Annalen*, 263, 283 (1891).

<sup>1</sup> Engl. Pat., Arthur Smith, 16247, August 9, 1899.

<sup>2</sup> D. R. P. A. Smith, 112685, October 10, 1899.

<sup>3</sup> D. R. P. Adolf Luft, 140552, April 29, 1902; U. S. P. 735278.

patent specifications, is to obtain a mass which remains "transparent and more or less plastic." After pouring his mixture in a suitable mold he dries at a temperature of about 50° C. He too insists on the advantages of using solvents and in his German patent (page 1, line 44) he states that from 2 to 10 per cent. glycerine must remain in the mass; moreover he arranges matters so as to retain in his mixture all the expensive camphor. The whole process of Luft looks clearly like an attempt to make a plastic similar to celluloid and to prepare it and to use it as the latter. The similarity becomes greater by the use of camphor and the same solvents as in the celluloid process.

I have prepared Luft's product; it is relatively brittle, very much less tough and flexible than celluloid; it does not melt if heated although it softens decidedly; acetone swells it and suitable solvents can extract free camphor and glycerine from it.

And now we come to an attempt of another kind, namely the formation of soluble synthetic resins, better known as shellac substitutes.

Blumer<sup>1</sup> boils a mixture of formaldehyde, phenols and an oxyacid, preferably tartaric acid and obtains a fusible, alcohol-soluble, resinous material, which he proposes as a shellac substitute. This substance is soluble in caustic soda lye; it can be melted repeatedly, and behaves like any soluble fusible natural resin. Blumer in his original English patent application puts great stress on the use of an oxyacid and seems to think that the latter participates prominently in the reaction; he uses it in the proportion of one molecule of acid for two molecules of phenol and two molecules of formaldehyde.

Nathaniel Thurlow, working in my laboratory on the same subject, has conclusively shown several years ago that the identical material can be obtained by the use of minute amounts of inorganic acids; he has shown furthermore that equimolecular proportions are not necessary; in fact they are wrong and harmful if the reaction be carried on in such a way that no formaldehyde be lost; he showed also that in order to obtain a fusible soluble resin, an excess of phenol over equimolecular proportions must be used, unless some formaldehyde be lost in the reaction.

So as to avoid confusion, I ought to mention here that Blumer and Thurlow's resin is relatively very brittle, more so than shellac and that no

amount of heating alone changes it into an insoluble, infusible product.

As to the real chemical constitution of this interesting product which I have tried to establish by indirect synthesis, I shall read a paper on this subject at one of the next meetings of this society.

About a year later, Fayolle<sup>1</sup> tries to make gutta-percha substitutes by modifying Luft's method: he adds large amounts of glycerine to the sulphuric acid used as condensing agent, and obtains a mass that remains plastic and can be softened and kneaded whenever heat is applied. On trial, this method gave me a brittle unsatisfactory substance of which it is difficult, if not impossible, to wash away the free acid without removing at the same time much of the glycerine. In this relation, Luft's way of adding the glycerine after eliminating the acid, seems more logical.<sup>2</sup>

Later,<sup>3</sup> the same inventor modified his method by adding a considerable amount of pitch ("brai") and oil thus trying to make another gutta-percha substitute which also softens when heated and remains plastic.

In 1905 Story<sup>4</sup> modifies all above methods in the following way: He discontinues the use of condensing agents and of added solvents; but he takes a decided excess of phenol, namely 3 parts of 40 per cent. formaldehyde and 5 parts of 95 per cent. cresol or carboic acid; by this fact the latter is present in excess of equimolecular proportions. He boils this mixture for 8-10 hours, then concentrates in an open vessel which drives off water and some formaldehyde, and which increases still more the excess of phenol; after the mixture has become viscous he pours it into suitable molds, cools down and afterwards hardens by slow *drying* below 100° C., or as stated in his patent, at about 80° C. His product is infusible and insoluble. But this method has some very serious drawbacks which I shall describe summarily and which Story himself recognized later.<sup>5</sup>

His process is necessarily slow. Leaving out of consideration his long preliminary boiling, the hardening process at temperatures below 100° C. is really a *drying* process where the excess of phenol that provisionally has acted as a solvent is slowly expelled. This assertion I have been able to verify beyond doubt by my direct experiments

<sup>1</sup> French Pat., E. H. Fayolle, 335584, September 26, 1903.

<sup>2</sup> See also addition patents to original French Pat. add. Pat. 2414, February 8, 1904 and 2485, February 18, 1904. Fayolle.

<sup>3</sup> French Pat., E. H. Fayolle, 341013, March 7, 1904.

<sup>4</sup> Engl. Pat., Henry Story, 8875, 1905.

<sup>5</sup> See his addition Patent, Belgium 210965, September 30, 1908.

<sup>1</sup> Engl. Pat., Louis Blumer, June 5, 1902, No. 12880.

where hardening was conducted in closed vessels at below  $100^{\circ}\text{C}$ . and where I succeeded in collecting phenol with the eliminated water. The evaporation or drying process may proceed acceptably fast for thin layers, or thin plates, but for masses of a somewhat larger volume, it requires weeks and months; even then the maximum possible hardness or strength is not reached at such low temperatures. All this not merely involves much loss of time, but the long use of expensive molds, a very considerable item in manufacturing methods; furthermore, during the act of drying, the evaporation occurs quickest from the exposed surface, thus causing irregular contraction and intense stresses, the final result being misshapen molded objects, rents or cracks.

Story states that if pure phenol be used the reaction proceeds very slowly; I should add that in that case the reaction does not take place, except very imperfectly, even after several days of continuous boiling. Even then in some of my own experiments made with pure commercial crystallized phenol and with commercial 40 per cent. formaldehyde, I obtained products not of the insoluble type, but similar to the soluble fusible products of Blumer and Thurlow.

Taken in a broad sense, Story's process is very similar to Luft's with this difference however, that he foregoes the use of an acid condensing agent and instead of using a solvent like alcohol, glycerine or camphor, he uses a better and cheaper one, namely an excess of phenol. In further similarity with Luft and Smith's his method is, as he expresses himself in his patent text, a *drying* process.

Like Smith and Luft he is very careful to specify temperatures *not* exceeding  $100^{\circ}\text{C}$ . for drying off his solvent.

Shortly after Story filed his patent, DeLaire<sup>1</sup> obtained a French patent for making soluble and fusible resins either by condensing phenols and formaldehyde in presence of acids, in about the same way as Blumer or Thurlow and then melting this product; or by dissolving phenol in caustic alkalies *used in molecular proportions*, then precipitating the aqueous solution with an acid and afterwards resinifying the reprecipitated product by heating it until it melts. I should remind you that the French patent laws allow patents without any examination whatever as to novelty. And I should state also that DeLaire simply uses here

the old and well-known processes of Lederer<sup>1</sup> and Manasse<sup>2</sup> which consists in making a phenol-alcohol by the action of formaldehyde on an aqueous solution of a phenolate and subsequent treatment with an acid.

It is a well-known fact that these phenol-alcohols, for instance saligenin, if heated alone or with an acid, will give partial anhydrides such as saliretin and homosaliretin,<sup>3</sup>  $\text{C}_{14}\text{H}_{14}\text{O}_3$  or  $\text{C}_6\text{H}_4(\text{OH})\text{CH}_2\text{OC}_6\text{H}_4\text{CH}_2\text{OH}$ ,<sup>4</sup> fusible and soluble in alcohol, or caustic soda, and precipitable from the latter by the addition of chloride of sodium.

Trisaligenosaligenin,  $\text{C}_{28}\text{H}_{26}\text{O}_5$  or  $4\text{C}_7\text{H}_8\text{O}_2 - 3\text{H}_2\text{O}$ ,<sup>5</sup> and heptasaligenosaligenin,  $\text{C}_{50}\text{H}_{50}\text{O}_9$  or  $8\text{C}_7\text{H}_8\text{O}_2 - 7\text{H}_2\text{O}$ ,<sup>6</sup> are both higher anhydrides of similar resinous character, the first one obtained by the action of sulphuric acid on saligenin, the latter by the action of acetic anhydride.

The direct homolog of saliretin, which is methylsaliretin or homosaliretin, has properties similar to saliretin, melts at  $200^{\circ}$  or  $205^{\circ}\text{C}$ . and is less soluble.<sup>7</sup>

No wonder then if the English<sup>8</sup> and the German patents<sup>9</sup> of DeLaire vary considerably in text and claims from the French patent; the claims are reduced merely to a method consisting in resinifying phenol-alcohols by heating them under reduced pressure or vacuum. The resins of DeLaire are fusible, soluble products, having all the general properties of saliretin and homosaliretin.

In order to complete my enumeration of methods where alkalies are used, I ought to mention two processes which aim at products very different from those which we have in view. Speyer<sup>10</sup> produces an antiseptic which easily gives off  $\text{CH}_2\text{O}$ . For this purpose he uses naphthol or polyphenols like resorcin or pyrogallol and adds an excess of ammonia and of formaldehyde. This gives him an insoluble powder which easily liberates  $\text{CH}_2\text{O}$  and  $\text{NH}_3$ . It is a well-known fact that ammonia reacts on formaldehyde and produces hexamethylentetra-

<sup>1</sup> *Journal Praktische Chemie* [2], vol. 50, page 224.

<sup>2</sup> *Ber.*, 1894, 2409-2411; D. R. P. Bayer, 85588; U. S. P., Manasse, 526786, 1894.

<sup>3</sup> Beilstein, *Organ. Chemie*, Vol. 2, 1896, page 1109.

<sup>4</sup> R. Piria, *Ann. Chem.*, **48**, 75; **56**, 37; **81**, 245; **96**, 357. Moitessier, *Jahresbericht*, 1886, page 676.

<sup>5</sup> K. Kraut, *Ann. Chem.*, **156**, 123; Gerhardt, *Ann. Chim. Phys.* [3], 7, page 215.

<sup>6</sup> F. Beilstein and F. Seelheim, *Ann. Chem.*, 117, page 83.

<sup>7</sup> C. Schotten, *Berichte*, 1878, page 784.

<sup>8</sup> *Engl. Pat.*, DeLaire, 15517, 1905.

<sup>9</sup> D. R. P., DeLaire, 189262, July 19, 1905.

<sup>10</sup> D. R. P., Arthur Speyer, 99570, November 2, 1897.

<sup>1</sup> French Pat., DeLaire 361539, June 8, 1905.

min,  $C_6H_{12}N_4$ ,<sup>1</sup> which easily acts upon acids and forms again  $CH_2O$ ,  $NH_3$  and methylamin.<sup>2</sup>

Two recent patents relate directly to the manufacture of soluble fusible resins. One of Farbenfabriken Fried. Bayer & Co.<sup>3</sup> uses orthocresol so as to obtain an odorless shellac substitute.

The other issued to Grognot<sup>4</sup> also for a shellac substitute, adds glycerine first, then after the reaction is over distills the solvent off.

After I had filed my own patent claims in the U. S. which gave me International Convention privileges, Helm<sup>5</sup> described, after me, amines or ammonium salts as condensing agents for the manufacture of synthetic resins with phenols and formaldehyde. He does not clearly indicate the chemical or physical properties of his resins. He furthermore makes the rather ambiguous statement that ammonium nitrate can be used as well as aniline. I have shown (see below) that in the case of ammonium nitrate the end-product may be a fusible soluble resin, while in the case where aniline is used I obtain finally an insoluble infusible resin.

It is true that Helm uses large amounts of aniline and nitrate of ammonium; his indicated proportions are very close to molecular proportions and this undoubtedly has, as I will show later, a great influence on the nature of the resulting products.

Knoll,<sup>6</sup> who also applied for patents after the filing date of my U. S. patents, uses sodium sulphite or *neutral*, or *acid* or *alkaline* salts as condensing agents; disregarding again the fact established by me, that according to whether an acid, a base, an acid salt, or an alkaline salt be used, the resinous products may be totally different.

This will close my review of the work done by others and I shall begin the description of my own work by outlining certain facts, most of which seem to be unknown to others, or if they were known their importance seems to have escaped attention. Of these facts I have made the foundation of my technical processes.

As stated before, the condensation of phenols with formaldehyde can be made to give, according to conditions and proportions, two entirely differ-

ent classes of resinous products. *The first class* includes the products of the type of Blumer, DeLaire, Thurlow, etc. These products are soluble in alcohol acetone or similar solvents, and in alkaline hydroxides. Heating, simply melts them and they resolidify after cooling. Melting and cooling can be repeated indefinitely but further heating will not transform them into products of the second class. They are generally called "*shellac substitutes*," because they have some of the general physical properties of shellac.

The second class includes the products of Kleeberg, Smith, Luft, Story, Knoll as well as my own product, in so far only as their general properties are concerned; but each one of them may be characterized by very distinct specific properties which have a considerable bearing on any technical applications. Broadly speaking, this second class can be described as infusible resinous substances, derived from phenols with aldehydes; some of them are more or less attacked by acetone, by caustic alkalies or undergo softening by application of heat. *At least one of them* is unattacked by acetone and does not soften even if heated at relatively high temperatures. None of them can be re-transformed into products of the first class even if heated with phenol.

These insoluble infusible substances can be produced directly in one operation by the action of formaldehyde on phenols under suitable conditions, for instance the process of Kleeberg (see above). Or they may be produced in two phases (see Luft and Story above), the first phase consisting of an incomplete reaction giving a viscous product that is soluble in alcohols, glycerine, camphor or phenol, and which on further heating or after driving off the solvent may gradually change into an infusible product.

In order to be able to stop at the first phase, the condensing agents may either be omitted (see Story above) or they may be used moderately (see Luft above) or they may be diluted with suitable solvents, for instance methyl- and amyl-alcohol (see Smith above) or with glycerine (see Fayolle above).

In all these processes there is a further treatment by which the solvent is driven off during a *drying* process. For example, in the process of Smith or Luft, alcohol or glycerine is thus expelled partially; and in Story's process the excess of phenol is driven off in the same way by slow

<sup>1</sup> Wohl, *Ber.*, **19**, 1892; Tollens, *Ber.*, **17**, 653.

<sup>2</sup> See also Moschatos and Tollens, *Ann. der Chemie.*, **272**, 280.

<sup>3</sup> D. R. P., Farbenfabriken vorm. Friedr., Bayer & Co., 201,261, April 16, 1907.

<sup>4</sup> L. Grognot, U. S. P. 391436, 1908.

<sup>5</sup> Engl. Pat., Louis Helm, 25216, November 13, 1907.

<sup>6</sup> Eng. Pat., Knoll & Co., 28009, December 19, 1907; Swiss Pat., Ditto, 40994, December 7, 1907.

drying under  $100^{\circ}\text{C}$ . In all these drying processes, some of the solvent is left, either purposely, so as to insure flexibility or plasticity, or it is left involuntarily, because at temperatures of  $100^{\circ}\text{C}$ . or below it is impossible to expel the totality of these solvents, part of which are stubbornly retained by the mass.

If I except the processes of Blumer, Thurlow or DeLaire, and generally those which have in view fusible and soluble resins, in all above-mentioned patent specifications temperatures of  $100^{\circ}\text{C}$ . or much below are insisted upon.

And yet I have convinced myself by often repeated experiments that temperatures above  $100^{\circ}\text{C}$ . and considerably above  $100^{\circ}\text{C}$ . are best suited or indispensable for the complete and rapid transformation into a final insoluble, infusible product of exceptionally desirable qualities. If this be so why have my predecessors not used temperatures above  $100^{\circ}\text{C}$ .?

Why do some of them recommend temperatures as low as  $80^{\circ}\text{C}$ . (Story) and even  $50^{\circ}\text{C}$ . (Luft)? Why do they prefer to make this final hardening a long and slow operation which does not give the best, the hardest, the most resisting product? (See confirmation of my statement by Story in Belgian addition patent 210965, September 30, 1908.)

For the simple reason that if their initial mass be heated at too high a temperature it gives off gaseous products, mainly composed of formaldehyde; this produces bubbles in the mass, makes it spongy, porous, and unfit for commercial use.

More direct experiments have proved to me that during the first stages of the process, we have to deal with a phenomenon that has all the characteristics of chemical dissociation with liberation of  $\text{CH}_2\text{O}$ .

If the initial mass be heated at temperatures above  $100^{\circ}\text{C}$ . the tension of this gas becomes very pronounced. At  $100^{\circ}\text{C}$ . the tension may become as high as 1 kilogram per square centimeter (above atmospheric pressure), but this tension subsides as soon as the final product is formed.

I shall explain later how I have utilized this knowledge to good advantage, and how I counteract this dissociation simply by exercising a compensating external pressure.

In the historical part of my paper, reference has repeatedly been made to the use of condensing

agents. We have seen how Kleeberg, Smith, Luft, Fayolle, Blumer and Thurlow use acid condensing agents. Others like Speyer, Hentsche, Lederer, Manasse, DeLaire, use alkalies, but every time in relatively large proportions: practically one molecule or over; but the products thus obtained are of a nature very different from the substance I am about to describe.

Story, on the other hand, adds no condensing agents whatever. True, he is able, with commercial impure carbolic acid, to obtain a reaction after about 8-10 hours' boiling, and this heating process has then to be supplemented by much longer drying. But if his process be carried out with pure or crystallized phenol, it takes many days of continuous boiling before a reaction sets in; even then the product obtained is of a dubious character hovering between a resin of class one (fusible and soluble) and a resin of class two (infusible and insoluble). It is more likely to be a fusible and soluble resin if for some reason or another the process has been carried out with an excess of phenol or if, some way or another, too much  $\text{CH}_2\text{O}$  has escaped in the after concentration. For instance by following his description and boiling for 5 days in a return condenser a mixture of 50 gr. pure crystalline phenol and 30 gr. 40 per cent. commercial formaldehyde, then concentrating in an open dish, I obtained the fusible soluble resin of Blumer or Thurlow which on further heating remains fusible and does not change into the insoluble infusible product as described by Story. I obtain the same result if the boiling be carried on in presence of a small amount of any acid, any acid salt, or any salt which on hydrolyzing may split, so as to give a preponderant acid reaction. This effect is shown by salts of mineral acids and heavy metals; it is shown even with ammonium chloride, and on acting upon formaldehyde liberates free hydrochloric acid.<sup>1</sup>

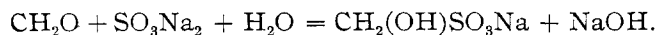
On the other hand, if I use an alkaline salt or a salt, which on hydrolyzing splits into a weak acid and a strong base, as for instance sodium acetate, I obtain under the same circumstances a resin of the insoluble, infusible variety even if to some extent, a slight excess of phenol has been used, showing conclusively that within certain limits the amount of phenol does not change the general character of the reaction. All what may happen in that case is that the final product is rendered impure by some excess of phenol which can be

<sup>1</sup> See Cambier, Brochet, *Compt. rend.*, 120, 557.

driven off afterwards by a drying process similar to that of Story.

I have obtained similar results with many other alkaline salts as for instance ammonium carbonate, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, borax, potassium cyanide, sodium silicate, soap, etc.

In the same way I have used sodium sulphite, which on acting on  $\text{CH}_2\text{O}$  liberates sodium hydroxide according to following reaction:



I might say that a similar effect is obtained from all substances which can act directly or indirectly as bases.

In other terms: *the quality as well as the quantity* of condensing agent has an enormous influence on the nature of the final products.

For the manufacture of insoluble, infusible, condensation products of formaldehyde and phenol, bases used in moderate amounts have very decided advantages. They accelerate the reaction without degenerating same into a violent and irregular process. The relatively small amount of base which may remain present in the finished product, either in combined or uncombined form, does not involve the same objectionable features for its technical uses as the presence of free acid.

Furthermore, for some reason or another acid condensing agents seem to favor the formation of soluble and fusible resins, while for some other reason, bases seem to favor the formation of insoluble, infusible resins.

Moreover, by the use of small amounts of bases, I have succeeded in preparing a *solid* initial condensation product, the properties of which simplify enormously all molding operations as we shall see later.

I have tried all organic or inorganic bases which I could obtain readily. I have tried the hydroxides and carbonates of the alkali metals, the hydrates of alkaline earths, ammonia and its alkaline salts, hydroxylamin, organic amines, pyridine, carbamide and other amides of weak acids; and the effect, with slight variations, is always about the same; it is quite natural, that for reasons of economy or expediency, I should prefer the commercially more available bases.

I wish it distinctly understood that in order to obtain my technical effect I use the bases in relatively small quantities, say less than one-fifth

of the amount which would be required to transform the phenol into phenolate.

If larger amounts of base be used, the results are technically much inferior; in fact the process changes gradually into such as give phenol-alcohols or compound condensation products of ammonia or amines with formaldehyde, all products very different from those I desire to make.

I have good reason to believe that in my process the bases only act as catalyzers and intervene only temporarily in the reaction. They seem to be expelled in free condition during the last stage of the process. For instance if I use ammonia, I find this ammonia back in the free state in the final hard condensation product.

A careful study of the condensation process of phenols and formaldehyde, made me discover that this reaction instead of occurring in two stages can be carried out in three distinct phases. This fact is much more important than it appears at first sight. Indeed it has allowed me to prepare a so-called *intermediate condensation product*, the properties of which simplify still further my methods of molding and enlarge very much the scope of useful applications of my process.

The three phases of reaction can be described as follows:

First phase. The formation of a so-called *initial condensation product* which I designate as *A*.

Second phase. The formation of a so-called *intermediate condensation product*, which I designate as *B*.

Third phase. The formation of a *final condensation product*, which I designate as *C*.

As to the properties of each of these condensation products I can define them in a few words:

*A*, at ordinary temperatures, may be liquid, or viscous, or pasty, or solid. Is soluble in alcohol, acetone, phenol, glycerine and similar solvents; is soluble in  $\text{NaOH}$ . *Solid A* is very brittle and melts if heated. All varieties of *A* heated long enough under suitable conditions will change first into *B* then finally into *C*.

*B* is solid at all temperatures. Brittle but slightly harder than solid *A* at ordinary temperatures: insoluble in all solvents but may swell in acetone, phenol or terpeneol without entering into complete solution. If heated, does not melt but softens decidedly and becomes elastic and somewhat rubber-like, but on cooling becomes again hard and brittle. Further heating under suitable conditions changes it into *C*. Although *B* is

infusible it can be molded under pressure in a hot mold to a homogeneous, coherent mass, and the latter can be further changed into *C* by the proper application of heat.

*C* is infusible, insoluble in all solvents; unattacked by acetone, indifferent to ordinary acids, or alkaline solutions; is destroyed by boiling concentrated sulphuric acid, but stands boiling with diluted sulphuric acid; does not soften to any serious extent if heated, stands temperatures of 300° C.; at much higher temperatures begins to be destroyed and chars without entering into fusion. It is a bad conductor of heat and electricity.

The preparation of these condensation products *A* and *B* and their ultimate transformation in *C* for technical purposes constitute the so-called Bakelite process. This can be described easily:

I take about equal amounts of phenol and formaldehyde and I add a small amount of an alkaline condensing agent to it. If necessary I heat. The mixture separates in two layers, a supernatant aqueous solution and a lower liquid which is the initial condensation product. I obtain thus at will, either a thin liquid called *Thin A* or a more viscous mass, *Viscous A* or a *Pasty A*, or even if the reaction be carried far enough, a *Solid A*.

Either one of these four substances are my starting materials and I will show you now how they can be used for my purposes.

If I pour some of this *A* into a receptacle and simply heat it above 100° C., without any precaution, I obtain a porous spongy mass of *C*. But bearing in mind what I said previously about dissociation, I learned to avoid this, simply by opposing an external pressure so as to counteract the tension of dissociation. With this purpose in view, I carry out my heating under suitably raised pressure, and the result is totally different.

This may be accomplished in several ways but is done ordinarily in an apparatus called a Bakelizer. Such an apparatus consists mainly of an interior chamber in which air can be pumped so as to bring its pressure to 50 or better 100 lbs. per square inch. This chamber can be heated externally or internally by means of a steam jacket or steam coils to temperatures as high as 160° C. or considerably higher, so that the heated object during the process of Bakelizing may remain steadily under suitable pressure which will avoid porosity or blistering of the mass.

For instance if I pour liquid *A* into a test tube and if I heat in a Bakelizer at say 160-

180° C., the liquid will change rapidly into a solid mass of *C* that will take exactly the shape of its container; under special conditions it may affect the form of a transparent hard stick of Bakelite. It is perfectly insoluble, infusible, and unaffected by almost all chemicals, an excellent insulator for heat and electricity and has a specific gravity of about 1.25.

It is very hard, cannot be scratched with the finger nail; in this respect it is far superior to shellac and even to hard rubber. It misses one great quality of hard rubber and celluloid, it is not so elastic nor flexible. Lack of flexibility is the most serious drawback of Bakelite. As an insulator, and for any purposes where it has to resist heat, friction, dampness, steam or chemicals it is far superior to hard rubber, casein, celluloid, shellac and in fact all plastics. In price also it can splendidly compete with all these.

Instead of pouring liquid *A* into a glass tube or mold I may simply dip an object into it or coat it by means of a brush. If I take a piece of wood, and afterwards put it into a Bakelizer for an hour or so, I am able to provide it rapidly with a hard brilliant coat of Bakelite, superior to any varnish and even better than the most expensive Japanese lacquer. A piece of wood thus treated can be boiled in water for hours without impairing its gloss in the slightest way. I can dip it in alcohol or other solvents, or in chemical solutions and yet not mar the beautiful brilliant finish of its surface. But I can do better, I may prepare an *A*, much more liquid than this one, and which has great penetrating power, and I may soak cheap, porous soft wood in it, until the fibres have absorbed as much liquid as possible, then transfer the impregnated wood to the Bakelizer and let the synthesis take place in and around the fibres of the wood. The result is a very hard wood, as hard as mahogany or ebony of which the tensile- and more specially the crushing strength, has been considerably increased and which can stand dilute acids or water or steam; henceforth it is proof against dry rot. I might go further and spend a full evening on this subject alone and tell you how we are now bringing about some unexpected possibilities in the manufacture of furniture and the wood-working industry in general. But I intend to devote a special evening to this subject and show you then how with cheap soft wood we are able to accomplish results which never have been obtained even with the most expensive hard wood.



In the same way I have succeeded in impregnating cheap ordinary cardboard or pulp board and changing it into a hard resisting polished material that can be carved, turned and brought into many shapes. I might take up much more of your time by simply enumerating to you the applications of this impregnation method, with wood, paper, pulp, asbestos, and other fibrous and cellular materials; how it can be applied for fastening the bristles of shaving brushes, paint brushes, tooth brushes, how it can be used to coat metallic surfaces with a hard resisting protecting material; how it may ultimately supplant tin in canning processes; but I have no doubt that your imagination will easily supply you a list of possible technical uses even if I defer this subject for some other occasion.

As to Bakelite itself, you will readily understand that it makes a substance far superior to amber for pipe stems and similar articles. It is not so flexible as celluloid, but it is more durable, stands heat, does not smell, does not catch fire and at the same time is less expensive.

It makes excellent billiard balls of which the elasticity is very close to that of ivory, in short it can be used for similar purposes like knobs, buttons, knife handles, for which plastics are generally used. But its use for such fancy articles has not much appealed to my efforts as long as there are so many more important applications for engineering purposes.

Bakelite also acts as an excellent binder for all inert filling materials. This makes, that it can be compounded with sawdust, wood pulp, asbestos, coloring materials, in fact with almost anything the use of which is warranted for special purposes. I cannot better illustrate this than by telling you that here you have before you a grindstone made of Bakelite and on the other hand a self-lubricating bearing which has been run dry for nine hours at 1800 rev. per minute without objectionable heating and without injuring the quickly revolving shaft.

If I mix Bakelite with fine sand or slate dust I can make a paste of it which can be applied like a dough to the inside of metallic pipes or containers, or pumps, and after Bakelizing, this gives an acid proof lining very useful in chemical engineering.

Valve seats, which are unaffected by steam, steam-packing that resists steam and chemicals, have been produced in a similar way.

Phonograph records have been made with it, and the fact that Bakelite is harder than rubber, shellac, or kindred substances indicates advantageous possibilities in that direction.

For the electrical industry, Bakelite has already begun to do some useful work. There too its possible applications are numerous. Armatures or fields of dynamos and motors, instead of being varnished with ordinary resinous varnishes, can simply be impregnated with *A*, then put into a Bakelizer and everything transformed into a solid infusible insulating mass; ultimately this may enable us to increase the overload in motors and dynamos by eliminating the possibility of the melting or softening of such insulating varnishes as have been used until now. But the subject of dynamos and motor construction is only at its very modest beginnings and I prefer to mention to you what has been already achieved in the line of molded insulators of which you will find here several very interesting samples.

This brings me to the subject of molding Bakelite.

For all plastics like rubber, celluloid, resins, etc., the molding problem is a very important one. Several substances which otherwise might be very valuable are useless now because they cannot economically be molded. The great success of celluloid has mainly been due to the fact that it can easily be molded. Nitrated cellulose alone, is far superior in chemical qualities to celluloid, but until Hyatts' discovery, it could only be given a shape by an evaporation process and its applications were very limited. The addition of camphor and a small amount of solvent to cellulose nitrate was a master-stroke, because it allowed quick and economic molding.

In the same way white sand or silica would be an ideal substance for a good many purposes, could it be easily compressed or molded into shape and into a homogeneous mass. But it *cannot*; and therefore remains worthless. And that is the main difference between a *plastic* and a *non-plastic*. It so happens that Bakelite in *C* condition does not mold; it does not weld together under pressure even if heated; only with much effort is it possible to shape some kind of an object out of it, but somehow or another the particles do not stick well together; in other terms it is not a true plastic. Therefore the molding problem has to be solved in the anterior stages of the process. We have seen how

Smith, Luft, and Story tried to solve a similar problem by the admixture of solvents and subsequent evaporation, but we know now that these very solvents imply most serious drawbacks.

I have already shown you how I am able to mold and harden quickly by pouring liquid *A* into a mold and heating it in a Bakelizer. But even that method is much too slow for most purposes. Furthermore, molds cost money; any rubber or celluloid manufacturer will tell you that the item of molds represents a big portion of the cost of his plant. If an order for 10,000 pieces has to be delivered and it takes an hour for molding, it will require between three and four years to fill this order with one mold and if the mold costs \$100 it will require \$5000 for molds alone if the order has to be finished within 20 days. For that very reason I have devised my molding methods so as to use the molds only during the very minimum of time. I have succeeded in doing so in several ways. One of the simplest ways is the following:

As stated before, the use of bases permits me to make a variety of *A* that is solid although still fusible. The latter is as brittle as ordinary rosin and can be pulverized and mixed with suitable filling materials. A mixture of the kind is introduced in a mold and put in the hydraulic press, the mold being heated at temperatures preferably about or above 160–200° C. The *A* melts and mixes with the filler, impregnating everything; at the same time it is rapidly transformed into *B*. But I have told you that *B* does not melt, so the molded object can be expelled out of the mold after a very short time and the mold can again be refilled. All the molded articles are now in *B* condition; relatively brittle but infusible. At the end of the day's work or at any other convenient time all the molded articles are put in the Bakelizer and this of course without the use of any molds; in this way they are finally transformed in "*C*" Bakelite of maximum strength and hardness and resisting power.

The process can still be further simplified. Instead of using *A*, we can use *B* and mold it in the hot press where it welds and shapes itself. After a very short time, the *B* begins to transform into *C* and can now be expelled from the mold. If the transformation in *C* is not complete, a short after-treatment in the Bakelizer will finish everything. I have succeeded thus in reducing the molding to less than two minutes for small objects.

The valuable properties of *B* may be used in many other ways; for instance *A* may be poured into a large container and be heated slowly at 70° C. until it sets to a rubber-like mass and shows that it is transformed into *B*. This block of *B* if warm has very much the consistency of printers' roller-composition, but is brittle when cold. The warm flexible mass can now be removed from its container or, divided, cut, or sawed to any desired shape and the so-shaped articles can be simply placed in a Bakelizer; no melting nor deformation can occur, so we need no mold while maximum heat is applied to bring everything in condition *C*.

I could multiply these examples by numerous other modifications of my process but I believe that what I have said will be enough to convince you of its many uses; we are studying now applications of Bakelite in more than forty different industries on some of which I shall report on some future occasion.

The chemical constitution of Bakelite and the nature of the reactions which occur in the Bakelite process are problems which I have endeavored to solve. This subject is not by any means an easy one. Indeed, we have to deal here with a product that cannot be purified by crystallization nor other ordinary methods, which is insoluble, does not melt nor volatilize; in other terms, it is not a product which is amenable to our usual methods of molecular weight determination. Its chemical inertness makes it unfit for studying possible chemical transformations and unless my friends, the physico-chemists, will come to my aid, discover some way for establishing some optical properties or other physical constants, we are very much at a loss to establish the molecular size of my product.

But I have been so fortunate as to be able to obtain some insight into its chemical constitution by a rather round-about way: Indeed, I have succeeded in making Bakelite by indirect synthesis.

As stated previously, oxybenzylalcohol if heated at 150° C., or in presence of acids, gives various partial anhydrides, called saliretin, which may resinify further if heated at higher temperatures. Saliretin products are more or less soluble in alcohol and acetone and in NaOH solution, from which they may be reprecipitated by means of NaCl.

We have already seen that DeLaire in heating phenol alcohols in vacuum obtains soluble resins. But I have heated saligenin in sealed tubes under

pressure at 180° C. for 8 hours, with and without the addition of small amounts of ammonia. In both cases I obtain a substance which is hard when cold, but which softens when heated, but does not melt. It swells in acetone and in NaOH and dissolves partially. This substance is not my intermediate condensation product *B*, because no amount of heating can transform it in *C*.

If, however, I heat oxybenzylalcohol in presence of enough CH<sub>2</sub>O or its polymers in a sealed tube at 180° C. for 8 hours, I obtain a substance entirely similar to Bakelite in properties and in chemical composition.

By varying the proportions and repeating the experiment a great number of times I succeeded in establishing that, unless I use at least 1 molecule of CH<sub>2</sub>O for 6 molecules of oxybenzylalcohol I do not obtain Bakelite but a product containing saliretin compounds.

The same result occurs by heating 6 molecules of phenol and 7 molecules of CH<sub>2</sub>O in presence of a small amount of a base.

If I use somewhat less formaldehyde or if for some reason or another all the formaldehyde does not enter into reaction, I obtain a substance which may still be attacked by acetone, probably because it contains uncombined phenol or saliretins after the reaction is over.

But I have found that all these substances, whether they are obtained by heating 6 molecules of phenol alcohol with at least one molecule of CH<sub>2</sub>O, or whether they are obtained by the action of phenol on formaldehyde under heat and pressure in presence of small amount of bases, can be purified and brought to about constant composition as follows:

The substance is pulverized, washed with 5 per cent. KOH solution, with dilute HCl, with alcohol, with acetone and finally dried to constant weight in *vacuo*.

The powder so obtained still contains traces of potassium, which I did not succeed in eliminating. The amount of same is very small, about 0.09 per cent. of ash, but it seems to cling tenaciously to the product and makes it somewhat hygroscopic making weighing for analytical purposes very difficult, and accounts for some variations in the results.

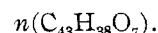
The organic combustion of all these products gave the following results:

1 mole CH <sub>2</sub> O.....	}	C = 77.48	77.88
6 mole saligenin.....		H = 5.96	5.97
		O = 16.56	16.15

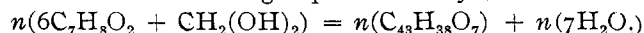
1 mole CH <sub>2</sub> O.....	}	C = 76.47	76.35
4 mole saligenin.....		H = 5.44	5.40
		O = 18.09	18.25
13 mole CH <sub>2</sub> O.....	}	C = 76.59	76.57
12 mole saligenin.....		H = 5.97	5.97
		O = 17.44	17.46
1 mole phenol.....	}	C = 77.48	76.61
1 mole CH <sub>2</sub> O.....		H = 5.60	5.80
and 1 per cent. NH <sub>3</sub> .....		O = 16.92	17.59
10 cc. phenol.....	}	C = 77.92	75.62
10 cc. 40 per cent. formaldehyde.....		H = 5.71	5.78
and ½ per cent. NH <sub>3</sub> .....		O = 16.37	18.60 <sup>1</sup>

If we take into consideration the great difficulties encountered in purifying methods, these results seem to indicate that we have to deal here with a definite organic substance of constant composition, which according to its methods of preparation may exist with impurities mixed in various proportions. These impurities are probably free phenol, or free CH<sub>2</sub>O or saliretin products.

From the indirect synthesis of Bakelite by means of oxybenzylalcohol and CH<sub>2</sub>O, I am led to consider Bakelite in its simplest form as a polymerized oxybenzyl—methylene—glycol—anhydride which, in case of ordinary phenol, might be represented by the following formula:



The reaction being represented by:



This formula corresponds acceptably to the analytical results if we take in consideration the difficulties of purification.

	C.	H.	O.
Calculated.....	= 77.44	5.75	16.81
Found (average).....	= 77.68	5.96	16.36
(with product of 6 mole saligenin + 1 mole CH <sub>2</sub> O).			

I consider Bakelite *C* as a direct polymer of another anhydride which is represented by my intermediate condensation product or Bakelite *B*. Bakelite *B* is a more complete anhydride than Bakelite *A*. As to Bakelite *A*, I am unable to arrive at a constant composition, for the reason that it easily gives off water, changing gradually its composition until heating converts it slowly into *B*, after passing through various mixtures of *A* and *B*.

My supposition has a strong appearance of probability by the following experiment:

If I put a mixture of phenol and formaldehyde in proper proportions and with some small amount of a base in a sealed glass tube and heat just long enough to produce *A* the formerly homogeneous liquid mixture separates into two layers. The initial condensation product *A* forms a lower stratum, and a supernatant layer of liquid indicates the elimination of water. The same thing occurs if

<sup>1</sup> Beginning oxidation during drying.

anhydrous phenol is heated with paraform in presence of a small amount of base.

If this *A*, first properly freed from any physically retained water, be introduced into another sealed tube and heated further, I may succeed, with some precaution as to the duration of heating, in stopping just in time so as to transform everything into *B*, the intermediate condensation product. I then see that a new amount of water is set free which will assemble on top, giving evidence of further dehydration. At the same time we notice that the mass *B* has not contracted in volume to any important extent.

If now this *B*, properly freed from water, be heated in another sealed tube, it will be transformed finally into *C*. But this time we see no further elimination of water. On the other hand there is a decided contraction of volume.

This contraction of volume, together with the remarkable increase in physical and chemical inertness, points out towards the probability that *C* is simply the polymer of *B*.

I am fully supported in this belief by the fact that analysis has shown me that *B* and *C* contain the same percentage of carbon, hydrogen and oxygen.

With homologs of phenol we obtain the direct homologs of these anhydrides; for instance with orthocresol we get the polymer of ortho-methyl-oxybenzyl-methylen-glycol-anhydride.

It may be of interest to remind you that many years ago, Oscar Low<sup>1</sup> called our attention to the great importance of formaldehyde as a starting point of synthesis in plant life. By the photochemical action of sunlight on CO<sub>2</sub> in presence of water in chlorophyll, oxygen is liberated and produces CH<sub>2</sub>O. This is the beginning of a process of further synthesis building up more complicated bodies.

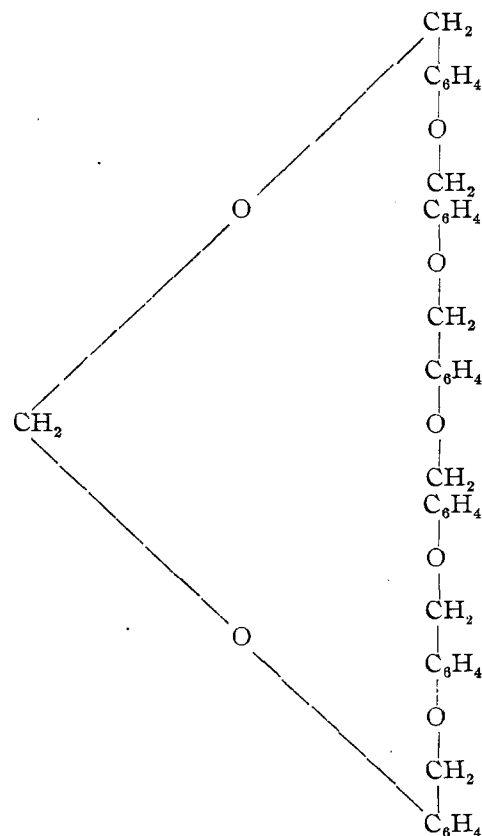
If we accept these premises then the theory of the Bakelite process is easy to explain:

Stage A.—Formation of a partial anhydride of a phenol alcohol and methylen glycol containing, hydroxyl groups, which can fix NaOH.

Stage B.—Formation of a higher anhydride by further elimination of water. This higher anhydride seems no longer to possess hydroxyl groups, but by addition of NaOH may still form alkaline compounds. This induces me to believe that in some

way or another we shall succeed in obtaining alkali compounds of the kind which on being treated with dilute acids will regenerate *A*.

Until we have anything better, I shall propose the formula:



Stage C.—Polymerization of the *B* product resulting in greater chemical inertness and disappearance of active corners of the molecule.

I shall also call your attention to the fact that the willow tree produces in its cells, salicin, which is the glucoside of saligenin; this same saligenin or oxybenzyl alcohol in presence of more CH<sub>2</sub>O has given me Bakelite.

On the other hand Bertrand,<sup>1</sup> and Vlchirch and Stevan<sup>2</sup> and more recently R. Majima and S. Cho<sup>3</sup> have called our attention to the phenolic nature of resinous substances, specially Japanese lacquer. The latter substance has some analogy with Bakelite and exudes from the *Rhus vernicifera* Dc. which is a plant that is somewhat related to our American "poison ivy."

<sup>1</sup> *Ann. Chim. Phys.* [6]. **12**, 115 (1898); *Bull. Soc. Chim.* [3]. **11**, 614 and 717 (1894).

<sup>2</sup> Tschirch und Stevan. *Arch. d. Pharm.*, **243**, 504 (1905).

<sup>3</sup> *Ber.*, **15**, November, 1907, page 4390.

<sup>1</sup> *Ber.*, **22**, 475 and **23**, 388 and 480.

So after all, the synthesis accomplished in my laboratory seems to have a decided similarity to some intricate biological processes that take place in the cells of certain plants.

In order not to increase too much the length of this paper, I have merely given you the brief outlines of years of arduous but fascinating work, in which I have been ably helped by Mr. Nathaniel Thurlow and more recently also by Dr. A. H. Gotthelf, who attended to my analytical work.

The opened field is so vast that I look forward with the pleasure of anticipation to many more years of work in the same direction.

I have preferred to forego secrecy about my work relying solely on the strength of my patents as a protection.

It will be a great pleasure to me if in doing so, I may stimulate further interest in this subject among my fellow chemists and if this may lead them to succeed in perfecting my methods or increase still further the number of useful applications of this interesting compound.

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(CONTRIBUTION FROM THE ARTHUR D. LITTLE LABORATORY OF ENGINEERING CHEMISTRY.)

### ACCURACY IN SAMPLING COAL.<sup>1</sup>

By E. G. BAILEY.

In 1899 the American Chemical Society was presented with a "Report of the Committee on Coal Analysis;" and so far as the chemical analysis is concerned the method recommended by this committee has been very closely followed by the majority of laboratories. In many specifications for the purchase of coal on the analysis and heat unit basis, it is stated that the sample shall be analyzed in accordance with the method adopted by the American Chemical Society, while the greater number of these specifications merely mention the sampling of the coal delivered and do not state definitely how the sample shall be taken and quartered down.

One specification covering the delivery of about 200,000 tons of coal per year states: "Sampling will be done by a representative of the company and contractor may have a representative present. Sample will be taken from each delivery and kept in hermetically sealed jars." Another specification on which almost twice this amount of coal is purchased describes the sampling as follows: "A small quantity of coal will be taken from each

weighing hopper just before the hopper is dumped, while the lighter is being unloaded. These quantities will be thrown into a receptacle provided for the purpose, and when the lighter is empty the contents of the receptacle will be thoroughly mixed, and a sample of this mixture will be taken for chemical analysis."

The specifications on which the United States Government purchase state: "Samples of the coal delivered will be taken by a representative of the Government. . . . The sample taken will in no case be less than the total of 100 pounds to be selected proportionally from the lumps and fine coal, in order that it will in every respect truly represent the quantity of coal under consideration.

"In order to minimize the loss in the original moisture content, the gross sample will be pulverized as rapidly as possible, until none of the fragments exceed one-half inch in diameter. The fine coal will then be mixed thoroughly and divided into four equal parts. Opposite quarters will be thrown out and the remaining portions thoroughly mixed and again quartered, throwing out opposite quarters as before. This process will be continued as rapidly as possible until the final sample is reduced to such amount that all of the final sample thus obtained will be contained in the shipping can or jar and sealed air-tight."

In one instance, the Government found 46.23 per cent. ash in a sample of coal delivered to a public building. The contract was based on 4.78 per cent. ash, and they obtained samples as low as 6.70 per cent., while the average for 10 samples was 11.58 per cent. ash. Referring to this instance, Mr. Woodwell, in a paper before the American Society for Testing Materials, says: "Moreover, the coal passed the visual inspection of officers charged with the duty of checking the weights and of noting the presence of slate, dirt, etc."

The United States Geological Survey has analyzed and tested some "bone coal," and their analyses show only 45.43 per cent. ash in West Virginia 11-B and 28.08 per cent. ash in West Virginia No. 24.

The "bands" or streaks of "bone coal" found in the Pittsburg seam as mined in West Virginia contain only 25 to 30 per cent. ash. A sample of "bone coal" from Pennsylvania was found to contain 30.56 per cent. ash. It is very difficult to conceive that a coal higher in ash than "bone coal" would be delivered by any coal company, and still more improbable that any inspector would not

<sup>1</sup> Read before the Industrial Division of Amer. Chem. Soc., Baltimore, December 31, 1908.