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RESIN AND METHOD OF PREPARING THE SAME.

No Drawing.

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The new methods relate to an improvement in the making of phenol formaldehyde condensation products (bakelite, etc.). Such products have been prepared heretofore from formaldehyde and cresol (or phenol). The cresol or the like is obtained from tar oil by means of an alkaline extraction in the well known manner.

According to the present invention ordinary tar oil can be used, as such, without separating hydrocarbons and acid constituents. This separation is performed by means of and simultaneously with the condensation with formaldehyde, leading to the production of resin.

Before describing the process proper, some experiments described by Gluud and Breuer in F. Fischer's *Gesammelten Abhandlungen zur Kenntnis der Kohle* 4,230, (1919-20) should be mentioned. These authors were the first ones to try the use of F. Fischer's low temperature tar (Urteer) for the making of condensation products (in laboratory experiments). They found that they could use crude low temperature tar which, by distilling, had been liberated from its highest boiling constituents. They observed that the hydrocarbons did not interfere with the reaction, but could be removed from the resinous products after the reaction had been completed. They (Gl. and B.) obtained, however, only unhardenable pitchlike resins in this way which could not be hardened by heating, and would be, therefore, of little practical value.

Another factor which would prevent a commercial adaptation of these experiments would be the impossibility of reproducing such effects with the ordinary "high temperature" tar which is generally on the market. Experiments were performed in which ordinary tar, liberated from its most viscous compounds was boiled with formaldehyde in the manner described by Gluud and Breuer; no separation of the layers as described by them was observed. With ordinary "high temperature" tar the hydrocarbons do interfere with the reaction; they stay in the final product and deteriorate its properties, making it unhardenable and pitchlike.

(At the same time control experiments were performed verifying Gluud and Breuer's statement concerning "low temperature" tar.)

The present invention, therefore, deals

with the condensation of "high temperature" tar and fractions thereof and describes the production of resins by a direct process which

1. Spontaneously separates the hydrocarbons.

2. Yields hardenable resins.

Several methods have been found which attain this end. The first one consists in adding to the coal tar or coal tar oil distilled from it, each containing tar acids, small amounts of hydrocarbons, preferably aliphatic hydrocarbons (mineral oil), or other solvents like chlorinated hydrocarbons, which do not dissolve the resin, have a specific gravity, smaller than water, and are miscible with the hydrocarbons of the tar oil. Such additions produce a separation of the hydrocarbons as is illustrated by the following experiment.

200 parts of 25% tar acid oil (from the Barrett Co. of New York) were mixed with 40 parts of commercial kerosene, 80 parts of 40% formaldehyde and 25 parts of a normal sodium hydroxide solution; the mixture was heated to boiling on a reflux condenser for half an hour. After that, on cooling, the mixture settled into three distinct layers, viz. 190 parts of an oily layer on the top, consisting essentially of hydrocarbons, 85 parts of an aqueous layer in the center, and 75 parts at the bottom of the vessel.

These three layers were separated and analyzed. The top layer proved to consist chiefly of volatile constituents; up to 250° Celsius 170 cc. distilled, after carrying on the distillation up to 300° a residue of about 7 parts of pitch remained. The distillate was then shaken with concentrated alkali in order to determine its content of acid constituents, this being 7%. This shows that by the condensation, the tar acids have been taken out by the tar oil (diminishing from 25 to 7%).

The resin, settling at the bottom of the reaction vessel, was heated and thus transformed into solid "A" which diminished its weight to 60 parts. It appeared as a thick brown mass, containing only little hydrocarbons. By sufficient heating it was transformed into the insoluble and infusible "C" which exhibited considerable hardness and toughness.

Trying to repeat this experiment without kerosene, no separation of layers was ob-

served, and a pitchlike unhardenable substance was obtained. This proves the importance of the addition of kerosene, or an allied solvent, as a new effective method in the condensation of tar oil.

Another method consists in carefully refining the tar oil containing tar acids and cutting out the lowest boiling fraction. In the case of "low temperature" tar, Gluud and Breuer found it sufficient to remove the most viscous constituents. With "high temperature" tar this is not sufficient, as proved above. The Barrett tar acid oil, used in the experiments, described above, is completely liberated from the most viscous compounds, more so that the products, used by Gluud and Breuer, as is proven by its boiling range which was found to be the following:

40% boiling up to 200°.

60% boiling up to 215°.

80% boiling up to 230°.

The rest up to 300°.

There was practically no pitch.

It was found that, if the tar oil containing tar acids is still further refined, it can be condensed with formaldehyde directly and the separation of the hydrocarbons may be obtained just as well without adding a solvent.

The following experiment may serve as an example:

By repeated distillation a low boiling tar oil containing tar acids was prepared from the Barrett oil, characterized by the following boiling range:

65% boiling up to 190°.

87% boiling up to 200°.

96% boiling up to 210°.

200 parts of this oil were boiled with 100 parts formaldehyde and 30 parts of normal hydroxide solution for 45 minutes. Although no solvent had been added, the mixture completely settled into three layers as described above.

The oily top layer was analyzed by distillation; it yielded a volatile oil containing 7% of acid constituent.

The resin, which settled at the bottom of the reaction vessel had excellent hardening properties. It resembled a bakelite resin, yet its mechanical properties appeared to be superior to bakelite owing to its greater elasticity and higher dielectric constants. This was found out by dissolving the resin in alcohol and producing coatings with it; also another part of it was used for impregnating moulding mixtures.

This experiment shows that by completely refining the tar oil, the separation of the resinous constituents and the noncondensable hydrocarbons can be attained. This is therefore another new and effective method for obtaining resins directly from tar oil.

Further experiments were performed with still lower boiling tar oil which yielded more

easily hardenable resins. From a number of such experiments it appeared that the best method would be in general, to use tar oils, having approximately the same boiling range as the cresol or phenol (the condensation of which is desired) contained therein.

The best results, as regards quality of the resins and separation of the layers, are obtained by combining the two above methods (adding of solvents and cutting out of the higher boiling constituents).

In condensing tar oil, as described, it is not possible in all cases to bring all the cresol, contained in the oil, into reaction. The oil, separated after the condensation on the top, may contain 5-10% acid constituents, especially so if little formaldehyde is used. The following method has been devised for extracting all cresols from the tar oil, without using an excess of formaldehyde.

A batch of tar oil is at first treated with formaldehyde and alkali in a reflux condenser as described, the amount of formaldehyde used being insufficient to combine with all of the phenols contained in the batch of oil. The resin product of the foregoing treatment consequently contains appreciable amounts of phenols and the oil layer also retains appreciable amounts of phenols. The said oil layer upon separation from the resin is again treated with formaldehyde and alkali, as before, but as the more readily extractable phenol content of the oil was removed in the first step, the resinous product of the second treatment contains free formaldehyde. Mixture of the resinous product of the first operation and the resinous product of the second operation affords an opportunity of a condensation reaction between the free phenols of one and the free formaldehyde of the other, thereby yielding a product which is relatively free from either phenols or formaldehyde. Of course, in this case, if the excess of formaldehyde in the resinous product of the second operation is greater than the excess of free phenols in the resinous products of the first operation (as is usually the case for the reasons heretofore explained) a corresponding amount of pure cresol or phenol will have to be added to the mixture of the two resinous products before the condensation step.

The oil layer from the second treatment after separation is preferably extracted with alkali in the usual manner to remove as far as possible the recoverable phenols in the original tar oil. The resultant solution containing alkali and phenol, may obviously be dealt with in any suitable manner for the recovery of the phenol or may be used as a part of the condensation agent in any of the preceding condensation treatments as heretofore described.

Intermediate between the second treat-

ment as above described and the final alkali extraction step, repeated successive treatments with new lots of formaldehyde may be introduced. Excess formaldehyde in the aqueous layers formed during any of the treatments may obviously be used in connection with new lots of tar oil.

Extraction of the phenols by means of formaldehyde condensation and by means of alkaline extraction may also be combined differently, e. g. by making one formaldehyde condensation and, after that, one alkaline extraction.

The hydrocarbons of the tar oil separated on the top of the aqueous phase after the condensation were shaken with dilute acid in order to remove basic constituents and redistilled. It was found that by this operation a colorless liquid with an agreeable smell was obtained, different from the hydrocarbons, separated from the tar oil by the old method of alkaline extraction. The hydrocarbons, separated after condensation, contain small amounts of esterlike substances which cause their agreeable smell. Owing to this property they are better suitable as solvents than ordinary hydrocarbons. This method of preparing hydrocarbons is another application of the new method of direct condensation.

The processes, described, can be produced in the same way by using other aldehydes instead of formaldehyde. Although the character of the resin is modified according to the aldehyde used, the separation of the layers takes place in the same way, the properties of the hydrocarbons (top oil) not being essentially affected.

I claim:

1. The method of forming phenol condensation products directly from coal tar oils which comprises mixing a coal tar oil containing tar acids with an aliphatic solvent, a solution capable of extracting the said tar acids from the tar oil and to catalyze the condensation reaction, and a solution containing an aldehyde-bearing material, heating said mixture until a reaction has occurred between the aldehyde and the phenols in said mixture, permitting the said mixture to separate into immiscible layers, the top layer being of an oily nature, the middle layer of an aqueous nature; and the bottom layer of a resinous nature, and withdrawing the said layers separately.

2. The method of forming phenol condensation products directly from coal tar oils which comprises adding a coal tar oil containing tar acids, kerosene, a caustic alkali solution, and a formaldehyde solution together to form a mixture, heating the said mixture until a reaction between formaldehyde and the phenols in said tar oils, causing a separation of said mixture into three immiscible layers, the top layer being of an

oily nature, the middle layer of an aqueous nature, and the bottom layer of a resinous nature, and separating the said layers from each other.

3. The method of forming phenol condensation products directly from coal tar oils which comprises adding a coal tar oil boiling below 300° C. containing tar acids, kerosene, a normal solution of caustic soda, and formaldehyde together to form a mixture, boiling said mixture until a condensation between formaldehyde and the phenols in said tar oils has occurred, continuing said boiling until the said condensation reaction is substantially complete, allowing the said mixture to separate into three immiscible layers, the top layer being of an oily nature, the middle of an aqueous nature, and the bottom of a resinous nature, and separating the said layers from each other.

4. The method of forming phenol condensation products directly from coal tar oils which comprises adding a coal tar oil boiling below 220° C. containing tar acids, a solution having the power to extract tar acids from the tar oil and to catalyze the condensation reaction of the said tar acids with an aldehyde, an aldehyde bearing substance, together, boiling said mixture until the condensation reaction between the said tar acids and the said aldehyde bearing material has occurred, then allowing said mixture to separate into three immiscible layers, the top layer having oily compounds therein, the middle layer having substances in aqueous solution, and the bottom layer having a hardenable resinous material, and separating said layers from each other.

5. The method as specified in claim 4 in which the condensation reaction occurs in the presence of an aliphatic solvent.

6. The method of forming phenol condensation products directly from tar oils which comprises treating tar oils containing tar acids with an alkaline solution and an aldehyde insufficient in amount to combine with all the tar acids, separating the mixture into three component parts, one part being of an oily nature containing tar acids, a second part being of an aqueous nature, and a third part being of a resinous nature, treating said oily part with further amounts of aldehyde and alkaline solutions, and repeating the aforesaid operations until substantially all of the tar acids have been removed from the tar oils.

7. The method of preparing a solvent from the direct condensation of tar oils which comprises treating tar oils containing tar acids with an alkaline solution and an aldehyde to cause a condensation reaction between the said tar acids and aldehyde, separating the oil having a density less than water from said mixture, and purifying said oil to produce a solvent.

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8. The method as specified in claim 7 in which the condensation reaction takes place in the presence of an aliphatic kerosene solvent.

5 9. The method of forming phenol condensation products directly from tar oils which comprises treating tar oils containing tar acids with an alkaline solution and an aldehyde insufficient in amount to combine
10 with all the tar acids, separating the mixture into three component parts, one part being of an oily nature containing tar acids, a second part being of an aqueous nature, and

a third part being of a resinous nature, treating said oily part with further amounts
15 of aldehyde and alkaline solutions, separating the resins formed in said preceding step, mixing the last mentioned resins with the resinous product of the treatment first described, and causing a condensation reaction
20 to occur between the free phenols contained in the resinous product of the first treatment and the free formaldehyde contained in the resins of said last mentioned treatment.

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8. The method as specified in claim 7 in which the condensation reaction takes place in the presence of an aliphatic kerosene solvent.
9. The method of forming phenol condensation products directly from tar oils which comprises treating tar oils containing tar acids with an alkaline solution and an aldehyde insufficient in amount to combine with all the tar acids, separating the mixture into three component parts, one part being of an oily nature containing tar acids, a second part being of an aqueous nature, and a third part being of a resinous nature, treating said oily part with further amounts of aldehyde and alkaline solutions, separating the resins formed in said preceding step, mixing the last mentioned resins with the resinous product of the treatment first described, and causing a condensation reaction to occur between the free phenols contained in the resinous product of the first treatment and the free formaldehyde contained in the resins of said last mentioned treatment.

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DISCLAIMER

1,658,281.—*Reinhard Beutner*, Louisville, Ky. RESIN AND METHOD OF PREPARING THE SAME. Patent dated February 7, 1928. Disclaimer filed December 13, 1929, by the assignee, *Aug. Nowack Aktiengesellschaft*.

Hereby disclaim from the scope of claim 4 of Patent No. 1,658,281 any method of forming phenol condensation products such as are set forth in said fourth claim of said patent in which the coal tar oil boiling below 220° C. is a coal tar oil derived from so-called low-temperature tar or a tar other than such as is derived from so-called high-temperature coal tar and has been distilled until substantially the whole of the distillate boils below 220° C.

The term low temperature tar as here employed is intended to refer to any tar obtained by the carbonization of coal in which,—when distilled by the standard method D20-18 of the American Society for Testing Materials, for the distillation of bituminous materials suitable for road treatment,—the total fraction of distillate coming over between the vapor temperatures of 170° and 300° C., shall comply with either of the following specifications: (a) the quantity of materials extractable from the distillate by a 10% sodium-hydroxide solution shall exceed 15% by volume, (b) the hydrocarbon portion of the said distillate remaining after the complete removal therefrom of tar acids and tar bases shall give, after exhaustive treatment with 98% sulphuric acid at room temperature, a sulphonation residue exceeding 10% of the tar acid free and tar base free hydrocarbons.

[*Official Gazette January 7, 1930.*]

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