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UNITED STATES PATENT OFFICE.

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PROCESS OF MAKING INDIGO.

SPECIFICATION forming part of Letters Patent No. 778,752, dated December 27, 1904.

Application filed December 9, 1902. Serial No. 134,522.

To all whom it may concern.

Be it known that we, RUDOLF KNIETSCH, a subject of the King of Prussia, German Emperor, PAUL SEIDEL, a subject of the King of Saxony, and OTTO J. GRAUL, a subject of the Duke of Anhalt, all residing at Ludwigshafen-on-the-Rhine, in the Kingdom of Bavaria, Empire of Germany, have invented new and useful Improvements in Processes of Manufacturing Indigo, of which the following is a specification.

In the specifications of Letters Patent No. 619,883, dated February 21, 1899, and No. 622,139, dated March 28, 1899, there is described the synthesis of indigo by treating phenyl-glycocoll or analogues thereof, their salts, ethers, and anhydrids with a body that effects the extraction of water and oxidizing the leuco compound obtained.

The method of obtaining artificial indigo in its unsulfonated form consisted in treating the phenyl-glycocoll body in a caustic-alkali melt. Caustic potash or caustic soda or a mixture of these two alkalies with one another were recommended for use, and it is further stated in the specification of Letters Patent No. 617,652, dated January 10, 1899, that quicklime may also be added to the alkali with good results. These inventions rendered it possible to prepare indigo starting from benzene, and as this hydrocarbon is both plentiful and cheap great hopes were entertained that the processes described in the said specifications would lead to the commercial manufacture of indigo from coal-tar on a large scale. In spite, however, of all the efforts made to make these processes a commercial success this proved impossible, because the yield of indigo obtained is too small. The best yield of indigo ever obtained from phenyl-glycocoll in the most successful experiments according to the processes described in the specification of the said Letters Patent No. 622,139, dated March 28, 1899, and in the specification of Letters Patent No. 617,652, dated January 10, 1899, was lower than twenty-five per cent. of that theoretically possible—that is say, more than seventy-five per cent. of the phenyl-glycocoll employed was destroyed or otherwise rendered unavailable for the reaction. Under these circumstances it was impossible to build up a commercial manufacture on the basis of the said Letters Patent, and the principal manufacture of artificial indigo that has hitherto been practiced uses phenyl-glycocoll-ortho-carboxylic acid as its initial material—that is, a body which is obtained commercially from the hydrocarbon naphthalene instead of from benzene.

We have made a series of researches extending over a long time, which have resulted in the discovery of improvements in the said processes which more than double the yield of indigo hitherto obtainable and render the commercial manufacture of indigo from the hydrocarbon benzene possible. In the researches referred to we have determined the effect of water and impurities in the alkaline melt on the course of the reaction. We have found that the presence of small quantities of water in caustic soda, when that is the alkali used in the melt, produces little or no effect upon the yield of indigo obtained—that is to say, the yield of indigo obtained when using caustic soda as free from water as it can be obtained commercially is not essentially greater than when using caustic soda containing, say, from five (5) to ten (10) per cent. of water; but we have found that there is a surprising difference when caustic potash, either alone or in admixture with caustic soda, is the alkali used in the melt, according as the melt is free from water or contains water. Thus when caustic potash containing from ten (10) to twenty (20) per cent. of water is used in the melt only one-quarter to one-half as much indigo is obtained as when caustic potash quite free from water is used. Further, it is stated in the aforesaid specification of Letters Patent No. 617,652, dated January 10, 1899, that quicklime may be added to the melt, thus assisting in bringing the phe-

nyl-gylcocoll body into admixture with the alkaline melt and, as is known, causing the operation to proceed more slowly and moderately and with a rather better yield. If no such body be present in the alkaline melt, the phenyl-glycocoll body has a tendency to form a liquid layer floating on the top of the melt and not mixing with it.

We have now found that the oxids of the alkali-earth metals besides this mechanical action exert a specific chemical action, in that a better yield of indigo is obtained when they are used, as hereinafter set forth.

In spite of the increased yield due to the use of caustic potash completely free from water this alone is not sufficient to render the manufacture of indigo from phenyl-gylcocoll possible. Further, caustic potash quite free from water is even to-day not an article of commerce. Our present invention is, however, based upon the peculiar behavior of caustic potash containing little or no water, as hereinbefore set forth, together with the specific action of an oxid or oxids of the alkali earths, for if a sufficient quantity of a dry oxid of an alkali-earth metal be added to the caustic-alkali melt containing water-free caustic potash or caustic potash that is nearly free from water the yield of indigo is so much increased that the commercial manufacture of indigo is rendered possible by this process. Thus if an alkali melt be taken composed of three thousand six hundred (3,600) parts of caustic potash and caustic soda in molecular proportions containing only about two and a half ($2\frac{1}{2}$) per cent. of water and one thousand (1,000) parts of quicklime and in this melt five hundred (500) parts of dry potassium salt of phenyl-glycocoll be added at a temperature of about two hundred and sixty-five degrees centigrade, (265° C.,) a yield of about fifty (50) per cent. of indigo is obtained. Such a mixture of caustic alkalies with this freedom from water can be obtained, for instance, by adding to the mixture of the ordinary commercial caustic potash and caustic soda the requisite quantity of sodium oxid. A similar mixture of the bodies obtained in any other way can of course be used; but it is desirable that no superoxid be present. If the mixture above stated be improved still further by reducing the quantity of water in it, the yield of indigo is still further increased. Further, the yields of indigo can be increased if more quicklime be added to the mixture; but the addition of a greater proportion of quicklime than that above stated is liable to cause difficulties in stirring the melt.

Again, if a caustic-alkali melt consisting of three thousand six hundred (3,600) parts of caustic potash and caustic soda in molecular proportions, containing about five (5) per cent. of water, and three thousand (3,000) parts of dry barium oxid be prepared and in this melt eleven hundred (1,100) parts of dry potassium salt of phenyl-glycocoll be melted at a temperature of about two hundred and sixty-five degrees centigrade, (265° C.,) in this case also the yield of indigo is about fifty (50) per cent. In this case also the yield is further improved if a lower percentage of water be present in the melt, and it is improved if a larger quantity of barium oxid be added.

In both the above examples a fifty (50) per cent. yield of indigo can be obtained with a caustic-alkali melt containing a higher percentage of water than that given in each case. If the amount of alkali-earth oxid be increased above that stated and in case barium oxid is used, the aforesaid difficulty in stirring occurs, only to a much smaller degree than with quicklime; but, on the other hand, quicklime is more easily obtained and is cheaper than barium oxid. Strontium oxid resembles quicklime in its action.

This invention is applicable to the manufacture of indigo from phenyl-glycocoll and its homologues tolyl-glycocoll and xylyl-glycocoll.

The following examples will serve to further illustrate the nature of our invention, which, however, is not confined to these examples. The parts are by weight.

Example 1: Mix together two hundred and ten (210) parts of caustic potash nearly free from water (containing, say, 3.1 per cent. of water) and one hundred and fifty (150) parts of caustic soda free from water with one hundred (100) parts of quicklime. Heat the mixture till a melt is obtained, and when this is uniform stir in at a temperature of two hundred and sixty to two hundred and sixty-five degrees centigrade (260° to 265° C.) about fifty (50) parts of the potassium salt of phenyl-glycocoll, maintaining the temperature for about one (1) hour, and work up the melt in the known manner.

Example 2: Mix together one hundred and fifty (150) parts of caustic soda, (free from water,) two hundred and ten (210) parts of caustic potash nearly free from water, (containing, say, 3.4 per cent. of water,) and three hundred (300) parts of barium oxid. Heat the mixture till a uniform melt is obtained, then add at a temperature of two hundred and thirty degrees centigrade (230° C.) one hundred and ten (110) parts of the potassium salt of phenyl-glycocoll. Maintain the temperature for about one (1) hour at two hundred and sixty to two hundred and sixty-five degrees centigrade (260° to 265° C.) and work up in the usual way.

It is impossible to give an example for the manufacture of indigo by the present invention, which shall be the cheapest and best for general application, because the economy of the process is dependent upon several elements which vary not merely from place to place, but also from time to time. Thus it must

depend upon the price of indigo what percentage yield is necessary in order that commercial manufacture be possible. Secondly, the expense incurred in obtaining potash free from water, or, as the case may be, in obtaining caustic potash freer from water than the ordinary commercial article, must be considered in determining the quality of potash that is to be used. Further, upon this factor, upon the yields obtained, and upon the relative price of barium oxid and quicklime will depend which of these oxids of the alkali-earth metals is to be employed. It may be said that under favorable circumstances a yield of about fifty per cent. of indigo from phenyl-glycocoll is one which would suffice to render the commercial manufacture possible, and we have therefore in the foregoing specification explained the conditions which must be observed to obtain this yield or a yield higher than this percentage, and from the data we have given the manufacturer in each locality will be able to calculate from the price at which he can obtain the materials in his factory which variation of the process will most economically give him the best yield of indigo.

We claim—

1. The improvement in the process of manufacturing indigo coloring-matters by a melt containing caustic potash and glycocoll derivative, which improvement consists in performing such melt under substantially anhydrous condition.

2. The improvement in the process of manufacturing indigo coloring-matters by a melt containing caustic potash and phenyl-glycocoll, which improvement consists in performing such melt under substantially anhydrous conditions.

3. The improvement in the process of manufacturing indigo coloring-matters by a melt containing caustic potash, glycocoll derivative and oxid of an alkaline-earth metal, which improvement consists in adding to said melt a proportion of said oxid in excess of that theoretically necessary to combine with all the water in the melt.

4. The improvement in the process of manufacturing indigo coloring-matters which consists in treating the glycocoll derivative with an oxid of an alkaline-earth metal in excess of that theoretically necessary to combine with all the water in the melt, and with caustic potash containing less than ten per cent. of water.

5. The improvement in the process of manufacturing indigo coloring-matters which consists in treating a glycocoll derivative with a barium oxid in excess of that theoretically necessary to combine with all the water in the melt, and with caustic potash containing less than ten per cent. of water.

6. The improvement in the process of manufacturing indigo coloring-matters which consists in treating a phenyl-glycocoll derivative with an oxid of an alkaline-earth metal in excess of that theoretically necessary to combine with all the water in the melt, and with caustic potash containing less than ten per cent. of water.

In testimony whereof we have hereunto set our hands in the presence of two subscribing witnesses.

RUDOLF KNIETSCH.
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Witnesses:
ERNEST F. EHRHARDT,
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