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MANUFACTURE OF DIBENZANTHRONE
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This invention relates to the manufacture of vat dyestuffs of the anthraquinone series. More particularly, this invention deals with an improved process for the manufacture of dibenzanthrone compounds by the alkaline fusion of benzanthrone or its derivatives.

The caustic fusion of benzanthrone to dibenzanthrone has received considerable study in the art. The earliest processes as suggested by Bally (U. S. Patent 818,992) involved the heating of benzanthrone in melted caustic potash at a temperature of 180 to 230° C. or the fusion of a benzanthrone derivative, for instance, chloro-benzanthrone, in a melt of equal parts of caustic potash and absolute alcohol at a temperature of about 150 to 180° C. (U. S. Patent 818,336). Later various modifications were applied to these original processes, most of them involving the addition of various diluents or assistants to the fusion bath. Among these, it has been claimed that the addition of reducing agents such as dextrine, dextrose, fructose and various aldehydes produce beneficial results. (U. S. Patents 1,478,027; 1,844,381; 1,845,246 and 1,849,826.) Nevertheless, the above processes leave much to be improved as regards quality of the product. Although the crude dyestuff obtained in many cases corresponds practically to the theoretical yield expected from the initial quantity of benzanthrone, the product is invariably contaminated with isodibenzanthrone, and its tinctorial value is low. In many cases the crude product contains as high as 40% of inert, vat-insoluble material, and the portion that is vatiable is frequently so rich in isodibenzanthrone as to seriously affect the shade of the dyeing, and render the dyestuff unfit for the purpose intended.

Most of these processes are in substance two-stage processes. At first 2,2'-dibenzanthronyl is formed (Houben, "Das Anthracen und die Anthrachinone", pages 774-775). The formation of this intermediate is particularly favored where the benzanthrone and caustic alkali are mixed in the cold and heated up jointly to the optimum fusion temperature. (The latter is generally around 180 to 230° C.) At the higher temperature, the intermediate ring closes to produce dibenzanthrone in leuco form, which upon aeration gives the dyestuff. It appears, however, that not all of the intermediate 2,2'-dibenzanthronyl is so ring closed. Under the influence of the higher temperature, part of the intermediate is disrupted and recombined in a

different manner to give isodibenzanthrone and other undesirable by-products.

I have now found that if benzanthrone is fused with alcoholic potash in the presence of an oxidizing agent, and preferably in the presence of an inhibitor such as potassium acetate, an exceptionally high yield of dibenzanthrone in a state of high purity may be obtained. The product obtained is generally quantitative in yield and substantially free of either vat insoluble impurities or isodibenzanthrone. The tinctorial yield of the product is 40 to 60% greater than that obtained by direct caustic fusion of benzanthrone, which is undoubtedly due both to the increased yield of dibenzanthrone and to its higher purity which causes its dyeings to be of true shade and improved brightness. Since an oxidizing agent is the direct opposite of a reducing agent, the above result is truly astonishing in view of the practice in the art as above referred to.

As oxidizing agent, practically any known agent adapted to work in alkaline medium may be employed. The field is practically unlimited, as both inorganic and organic oxidizing agents may be resorted to with great success. Thus, the following oxidizing agents have been found by me to give improved results: metallic peroxides; alkali metal chromates, bichromates, and permanganates; metal nitrates or chlorates; cupric oxides or salts; ferric compounds; nitrobenzene sulfonic acids.

With most oxidizing agents, best results are obtained if the agent is added after the beginning of the reaction and preferably at that stage when formation of 2,2'-dibenzanthronyl apparently proceeds at a high rate. In other words, the oxidizing agent should be added after the temperature of the mass has reached about 100°-150° C., and has been maintained at this temperature for some time. The rule, however, is not absolute and varies considerably with the particular oxidizing agent selected. Thus in the case of basic ferric acetate, I have added the entire oxidizing agent at the beginning, and before the mass was heated up to the optimum temperature. The fusion product, however, exhibited fully 40 to 60% greater tinctorial yield than dibenzanthrone obtained by direct fusion.

Inert diluents may be added if desired, for instance, kerosene, naphthalene, diphenyl, and the like.

The theory of the reaction is not quite understood. As stated above, it appears that 2,2'-dibenzanthronyl, more correctly, its leuco form, is

first formed in the reaction. The presence of the oxidizing agent apparently assists its conversion into leuco-dibenzanthrone, without giving it the opportunity to decompose, under the influence of the high temperature, into intermediate products which would otherwise lead eventually to iso-dibenzanthrone or to alkali-insoluble by-products. The latter effect is particularly brought out by the use of an inhibitor such as potassium acetate. This agent seems to regulate and slow down the rate of reaction whereby to prevent the formation of the undesirable by-products prior to the final heating up stage, where the oxidizing agent begins to exert its effect. Any other means of controlling the rate of reaction during the first stage of the process without, however, cooling the mass to a point where fusion will not proceed at all, would appear to give equally good results. For instance, sodium acetate, potassium propionate, or other alkali metal salts of lower aliphatic acids may be used to accomplish the same purpose.

The quantity of oxidizing agent required for improvement may vary within wide limits. The theoretical quantity appears to be the equivalent of $\frac{1}{2}$ atom of oxygen per mole of benzanthrone. However, allowance must be made for the fact that the oxygen equivalent of a given oxidizing agent in alkaline alcoholic medium is not the same as that in aqueous acid medium. Generally it is less, therefore a greater quantity of the oxidizing agent is necessary. Thus, in the case of potassium chlorate I found that $1\frac{1}{2}$ to $2\frac{1}{2}$ moles per mole of benzanthrone gives best results. In the case of potassium permanganate, as low as $\frac{3}{4}$ moles per mole of benzanthrone was sufficient. In the case of cupric oxide $4\frac{1}{2}$ moles were found necessary. Moderate excesses of oxidizing agent produce no ill effects upon the product.

I have also found it advantageous to use a lower alcohol-potash ratio than used heretofore in similar fusions in the art. Generally speaking, the ratio of alcohol to caustic potash should not exceed 1:2 by weight.

Without limiting my invention to any particular procedure, the following examples are given to illustrate my preferred mode of operation. Parts given are by weight.

Example 1

25 parts of fused potassium acetate are added to 25 parts of methanol and stirred until substantially dissolved. 150 parts of caustic potash are added, and the mass is heated to 125–130° C. 250 parts of molten naphthalene are now introduced, and then 50 parts of purified benzanthrone, M. P. 168–170° C., are added. The temperature is then raised at a uniform rate to 140° C. during half an hour. There are then added 50 parts of finely ground natural manganese dioxide (approximately 86% MnO_2) during 5–10 minutes. Heating is continued uniformly to a gentle reflux (about 215°) and held at this temperature with continued stirring for $\frac{3}{4}$ hour. After cooling to 85–90° C., 750 parts of warm water are added and the naphthalene is distilled off with steam. The residual mass in the still is then filtered and washed with water. The filter cake is suspended in 1500 parts of water; 150 parts of sulfuric acid (66° Bé.) and 35 parts of sodium bisulfite are added, and the mass brought to a gentle boil, filtered, washed and dried. A quantitative yield of dyestuff is thus obtained which is practically free of iso-dibenzanthrone, dissolves in concentrated sul-

furic acid with a red-violet color, and gives dyeings upon cotton of the shade characteristic of pure dibenzanthrone.

If in the above example, 25 parts of fused sodium acetate or 25 parts of fused potassium propionate are used instead of 25 parts fused potassium acetate, very similar results are obtained.

Example 2

250 parts of molten naphthalene, previously heated to 130–135° C. are added to a melt of 25 parts of methanol, 25 parts of fused potassium acetate and 150 parts of caustic potash flakes all previously heated to 125° C. 50 parts of benzanthrone are then added at the same temperature. The temperature is then raised at a uniform rate during about $\frac{3}{4}$ hour to 135° C., when 25 parts finely ground potassium permanganate are added. Heating is continued so that the temperature rises uniformly to a gentle refluxing of the naphthalene and the fusion mass is stirred at this temperature (210–215° C.) for $\frac{3}{4}$ hour and worked up as in Example 1. Dibenzanthrone is thus obtained in a very high tinctorial yield.

Example 3

260 parts of high boiling kerosene are heated to 130° C. and added to a melt of 25 parts of methanol, 25 parts of fused potassium acetate and 150 parts of caustic potash flakes, heated to 130° C. The temperature of the mixture is adjusted to 125° C., and 50 parts of benzanthrone are added. The whole mass is heated during about $\frac{3}{4}$ hour to 135° C., 50 parts manganese dioxide (86%) are then added during about 5–10 minutes and the temperature of the mass is raised to 220° C. during $\frac{1}{2}$ – $\frac{3}{4}$ hour. The fusion mass is maintained at a temperature of 215–220° C. for another $\frac{3}{4}$ hour; cooled to 150–160° C., and the kerosene layer is decanted off. The fusion mass is then transferred into cold water, steam distilled free of traces of kerosene, filtered and washed. The product, when freed of manganese compounds as in Example 1, consists of dibenzanthrone exceptionally free from impurities.

Example 4

The fusion is carried out as in Example 2, with the exception that 62.5 parts potassium chromate are used instead of 25 parts potassium permanganate, and the chromium hydroxide is removed after the fusion by a simple acid extraction. The product so obtained is practically of identical quality with that of the previous examples.

Example 5

50 parts of benzanthrone are added at 125° C. to a melt of 25 parts of methanol, 25 parts of fused potassium acetate, 150 parts of caustic potash flakes, and 250 parts of naphthalene, mixed hot in the order given. The temperature is then raised during about $\frac{3}{4}$ hour to 135° C. and 79 parts of finely powdered cupric oxide are added. Heating is continued so that the refluxing point (210–215° C.) is reached during about $\frac{3}{4}$ hour. After being maintained at this temperature for $\frac{3}{4}$ hour more, the fusion mass is allowed to cool with stirring to 85–90° C. and diluted with 600 parts warm water. After steam distillation of the naphthalene, copper is removed by known methods and the dyestuff filtered off and dried. Dibenzanthrone is thus ob-

tained of a quality practically identical with that of the products previously described.

Example 6

5 A melt of 50 parts of methanol, 25 parts of fused potassium acetate and 150 parts of caustic potash flakes is heated to 130° C. and then diluted with 250 parts of molten naphthalene. 50 parts of benzanthrone are then added at 125° C. and the temperature raised to 135° C. during about ¾ hour. 75 parts of finely powdered potassium dichromate are then added, the temperature is raised slowly to the refluxing point of the mixture, and maintained at that point with stirring for ¾ hour. The melt, which becomes very thick toward the end, is freed from naphthalene, by decantation, transferred to cold water, and steam distilled free of traces of diluent. After filtering and washing, chromium compounds are removed by extraction with dilute sulfuric acid. The product so obtained consists of dibenzanthrone having substantially the same properties as above noted.

Example 7

25 A melt of 37.5 parts of methanol, 12.5 parts of fused potassium acetate and 150 parts of caustic potash flakes is heated to 135° C. and diluted with 250 parts molten naphthalene. 50 parts of benzanthrone are then added at 125° C., and the temperature is raised during about ¾ hour to 135° C. 50 parts of finely powdered potassium chlorate are then added and the temperature is raised to the refluxing point (210–215° C.). After stirring ¾ hour at this temperature, the fusion mass is cooled to 125–130° C. and vacuum is gradually applied to the fusion kettle. The naphthalene distills over without foaming at 120–125° C. under 28 inches vacuum and is recovered in a pure anhydrous form suitable for re-use. The residue is stirred up in water, aerated, filtered, washed, and dried in the usual manner. Dibenzanthrone is thus obtained of substantially the same properties as described in the previous examples.

Similar results are obtained if potassium or sodium nitrate are used instead of potassium chlorate. The use of sodium chlorate also gives practically the same results as potassium chlorate with the exception that the recovery of diluent is somewhat diminished.

Example 8

55 A melt is prepared as in Example 7, using 15 parts of methanol, 15 parts of fused potassium acetate, 90 parts of caustic potash, and 150 parts of naphthalene. 15 parts of Bz2-methoxy-benzanthrone (obtained according to U. S. Patent No. 1,614,398) are then added at 125° C., and the temperature is raised to 135° C. during ¾ hour. After adding 15 parts of finely powdered potassium chlorate, heating is continued until a temperature of 190° C. is reached. The fusion mass is then stirred ¾ hour at 190–200° C. and worked up by cooling to about 125° C., drowning in 900 parts of cold water, followed by aeration, steam distillation of the naphthalene, filtration and washing. The product so obtained consists of dimethoxy dibenzanthrone having less than 3% vat-insoluble impurities.

Example 9

75 30 parts of benzanthrone and 30 parts of powdered potassium chlorate are added at 135–140° C.

to a melt of 30 parts of methanol, 7.5 parts fused potassium acetate and 90 parts caustic potash. The fusion mass is heated gradually to 210° C., allowing alcohol to distil off, and is held at 210–215° C. until dyestuff formation is complete, which usually requires ¾ to 1 hour. The melt may then be drowned in water, or cooled and diluted with water, aerated, filtered, washed, and dried. Dibenzanthrone of high purity and high tinctorial yield is so obtained.

Example 10

50 parts of benzanthrone are added at 125° C. to a melt of 50 parts of 95% ethyl alcohol, 25 parts of fused potassium acetate, 150 parts of caustic potash and 300 parts of naphthalene, mixed hot in the order given. After raising the temperature to 135° C. during ½–¾ hours, 62.5 parts of finely powdered potassium dichromate are added, and the temperature is then raised to 210° C. and maintained with continued stirring at 210–215° C. for ¾ hour. After cooling the melt to 85° C., it is diluted with 600 parts of warm water and worked up by steam distillation of the naphthalene, and extraction of chromium compounds by means of dilute sulfuric acid. The dyestuff so obtained consists of high grade dibenzanthrone of practically the same properties as described above.

Example 11

250 parts of molten naphthalene are added to a melt of 37.5 parts of methanol, 12.5 parts of fused potassium acetate and 150 parts of caustic potash heated to 130–135°. There are then added 50 parts of finely powdered basic ferric acetate and 25 parts of purified benzanthrone. The temperature is raised to the refluxing point of the mixture. After stirring for ¾ hour at this temperature (215° C.) the melt is allowed to cool to about 100° C. and diluted with 600 parts of warm water. The product is worked up by steam distillation to remove naphthalene, filtered, and the filter cake is boiled in an excess of hydrochloric acid to remove iron compounds. It is then filtered, washed and dried. The product so obtained consists of dibenzanthrone of substantially the same high qualities as above described.

Example 12

50 A melt of 37.5 parts of methanol, 12.5 parts of fused potassium acetate and 150 parts of caustic potash flakes is heated to 135° C. and diluted with 250 parts molten naphthalene. The temperature is then adjusted to 125° C. and 37.5 parts of finely ground basic ferric acetate and 25 parts of alpha-chlor-benzanthrone, obtained, for example, from alpha-chloranthraquinone and glycerine, are added. The temperature is then raised to about 215° C. and the reaction mixture stirred under reflux for ¾ hour. After cooling to 90–100° C., 600 parts warm water are added, and the naphthalene is removed by steam distillation. The product is isolated by filtering and washing, followed by extraction with hydrochloric acid to remove iron hydroxides. The dyestuff so obtained gives a somewhat greener shade of blue than dibenzanthrone itself and is of excellent yield and great purity.

It will be understood that many variations and modifications are possible in the preferred procedures above indicated without departing from the spirit of this invention.

Thus, instead of any of the oxidizing agents indicated above, many other oxidizing agents may

be used. In one test, following the procedure of Example 1, I have replaced the 50 parts of manganese dioxide by 85 parts of finely ground m-nitrobenzene-sodium sulfonate (68%) with highly satisfactory results. Mixtures of oxidizing agents are sometimes advantageous.

The proportion of alcohol may be varied somewhat, depending on the kind of alcohol and the kind of oxidizing agent, but the amount used should not be less than those indicated in the examples at risk of formation of more or less isodibenzanthrone. Generally, a ratio of $\frac{1}{6}$ to $\frac{1}{2}$ part of alcohol to each part of caustic potash will give satisfactory results, with an optimum at about 1:4.

It has been found that prolonged heating such as 3 to 4 hours, as specified in some of the older types of fusions, is not necessary, but that dyestuff formation is usually complete in $\frac{3}{4}$ to 1 hour after the maximum temperature of the fusion has been reached. The latter may vary between 180 and 230° C.

Instead of working up the fusion by steam distillation, a solvent for naphthalene, such as toluene, may be added to the partially cooled melt, followed by filtration and washing the filter cake with a light solvent to remove the heavier diluent. Alternatively, vacuum distillation may be resorted to, as illustrated in Example 7. After steam distillation of the diluent, the dyestuff may be separated from insoluble inorganic matter by vatting, filtering and aerating the filtrate.

Many other variations and modifications are possible without departing from the spirit of this invention.

I am aware of U. S. Patent No. 1,564,423, wherein benzanthrone is first converted to 2,2'-dibenzanthronyl and the latter is isolated and converted into dibenzanthrone or an oxidation derivative thereof either by further caustic fusion in the absence of an oxidizing agent or by oxidizing in acid medium. My novel process differs from the above in several important respects, of which the following two are of major significance. In my improved process no intermediate isolation steps are necessary, and the oxidation is effected in alkaline medium. That 2,2'-dibenzanthronyl could be ring closed by oxidation in alkaline medium has apparently not been known to date. On the contrary, as already pointed out above, it was believed in the art that the caustic fusion is favored by the presence of reducing media. I may add further, that the final dyestuffs obtainable by my process are of superior purity and tinctorial yield as compared with the dyestuffs when the procedure of said U. S. Patent No. 1,564,423 is followed.

I claim:

1. The process of producing a dibenzanthrone which comprises fusing a benzanthrone with alcoholic potash in the presence of an oxidizing agent.

2. The process of producing a dibenzanthrone which comprises fusing a benzanthrone with alcoholic potash in the presence of an oxidizing agent, the alcohol potash ratio being less than 1 to 2 by weight.

3. The process of producing a dibenzanthrone which comprises fusing a benzanthrone with alcoholic potash in the presence of an oxidizing agent, the alcohol potash ratio being less than 1 to 2 by weight, and the amount of oxidizing agent being not less than the alkaline equivalent of $\frac{1}{2}$ atom of oxygen per mole of benzanthrone.

4. The process of producing a dibenzanthrone

which comprises fusing a benzanthrone with alcoholic potash in the presence of an oxidizing agent and an alkali-metal salt of a lower aliphatic acid.

5. A process as in claim 4, the alcohol: potash ratio being less than 1:2 by weight, and the amount of oxidizing agent being not less than the alkaline equivalent of $\frac{1}{2}$ atom of oxygen per mole of benzanthrone.

6. A process for producing dibenzanthrone which comprises heating a melt of benzanthrone in alcoholic potash to a temperature between 100 and 150° C., adding an oxidizing agent and further heating the mass at a temperature favoring the formation of dibenzanthrone.

7. A process as in claim 6, the quantity of alcohol being less than $\frac{1}{2}$ by weight of the quantity of caustic potash.

8. A process as in claim 6, the fusion mass containing further an inert diluent.

9. A process as in claim 6, the fusion mass containing further naphthalene as a diluent.

10. A process as in claim 6, the fusion mass containing further an alkali metal salt of a lower fatty acid.

11. A process as in claim 6, the fusion mass containing further potassium acetate.

12. A process for producing dibenzanthrone which comprises heating a melt of benzanthrone in alcoholic potash to a temperature between 100 and 150° C., adding an oxidizing agent and further heating the mass at a temperature of between 180 and 230° C.

13. A process for producing dibenzanthrone which comprises preparing a melt comprising benzanthrone, alcohol, caustic potash, an oxidizing agent and an alkali metal salt of a lower aliphatic acid at a temperature not less than 100° C. and not above 150° C., and heating said melt further to a temperature between 180 and 230° C. until dyestuff formation is substantially complete.

14. A process as in claim 13, the quantity of alcohol being less than $\frac{1}{2}$ by weight of the quantity of caustic potash.

15. A process as in claim 13, the melt containing further an inert diluent.

16. The process of producing dibenzanthrone which comprises fusing benzanthrone in a melt of caustic alkali, an alcohol, an inert diluent and an alkali-metal salt of a lower aliphatic acid at a temperature of about 120 to 150° C., adding an oxidizing agent, raising the temperature to between 180 and 230° C. and continuing the heating until dyestuff formation is substantially complete.

17. The process of producing dibenzanthrone which comprises fusing benzanthrone in a melt of caustic potash, methanol, naphthalene and potassium acetate at a temperature of about 120 to 150° C., adding an oxidizing agent, raising the temperature to between 180 and 230° C. and continuing the heating until dyestuff formation is substantially complete.

18. A process as in claim 17, the alcohol being present in a ratio not less than $\frac{1}{6}$ and not more than $\frac{1}{2}$ by weight of the caustic potash.

19. A process for producing dibenzanthrone which comprises fusing benzanthrone in the presence of caustic potash under conditions favoring the formation of 2,2'-dibenzanthronyl, adding an oxidizing agent and further fusing the mass at a temperature favoring the formation of dibenzanthrone.

20. A process of producing dibenzanthrone

which comprises fusing a mixture of benzan-
throne, caustic potash, alcohol, an alkali metal
salt of a lower aliphatic acid and an oxidizing
agent under conditions favoring the formation
5 of 2,2'-dibenzanthronyl, and then raising the
temperature to the range favoring the formation
of dibenzanthrone.

21. The process of producing dibenzanthrone
which comprises oxidizing 2,2'-dibenzanthronyl
10 in alkaline medium.

22. The process of producing dibenzanthrone

which comprises oxidizing 2,2'-dibenzanthronyl
in its own highly alkaline mass of formation.

23. In the process for producing dibenzan-
throne which comprises fusing benzanthrone in
the presence of caustic potash under conditions
favoring the formation of 2,2'-dibenzanthronyl
5 and then adjusting the conditions to effect ring-
closure to dibenzanthrone, the step which com-
prises carrying out at least the latter part of the
fusion in the presence of an oxidizing agent. 10

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