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PROCESS FOR PRODUCING INDIGO

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This invention relates to the production of indigo and more particularly refers to the production of indigo in a very finely divided form, having much greater covering power than synthetic indigos heretofore known.

It is an object of the present invention to produce indigo in much more finely divided form than was heretofore possible. A further object is to produce indigo having a deeper color and greater covering power than the commercial product now so extensively used. Additional objects will appear hereinafter.

In order to produce a synthetic indigo which had a covering power and fineness of subdivision superior to synthetic indigos heretofore produced I have departed from the customary process, whereby indoxyl or leuco indigo was oxidized by blowing with air, and have produced a greatly superior product by an accelerated oxidation which will hereinafter be described.

There are numerous well known oxidizing agents, which may roughly be divided into organic and inorganic compounds. Many well known organic oxidizing agents were tried by me but had to be discarded since they interfered with the caustic recovery, which is an essential feature of any commercial synthetic indigo process. When it was sought to recover the caustic after oxidizing with organic agents it was found that these agents caused considerable foaming and in many cases required a carbonization to remove the organic matter. Naturally, this difficulty would prevent the wide-spread commercial use of such a process, so I next sought the answer to the problem by experimenting with inorganic oxidizing agents.

In carrying out these experiments I first used permanganates and dichromates, since they are among the best known of the inorganic oxidizing agents. Here too, I was met with difficulties, since it became necessary to remove the contaminating end products of the oxidizing agents from the indigo, which removal would be a tedius and very expensive adjunct to any commercial process. Ferricyanides were then experimented with but with no more success since they rendered the caustic filtrate impure and thereby greatly increased the cost of production of the indigo. As previously mentioned, any process for producing synthetic indigo which is to be commercially feasible must necessarily permit the ready recovery of caustic in an uncontaminated form.

From these experiments it would seem that any of the well known oxidizing agents, whether organic or inorganic, would present the same difficulties, namely, contamination of the indigo or contamination of the caustic by-product. However, upon experimenting further I was surprised to find that by the use of alkali metal hypohalites there was produced a very finely subdivided product having a covering power and extent of subdivision far superior to ordinary synthetic indigo; and in addition, the caustic by-product was easily recovered in uncontaminated condition. While I have found that alkaline earth metal hypohalites may also be used, I prefer to use the alkali metal hypohalites, particularly sodium hypochlorite, since the products resulting therefrom are even less contaminated than where the alkaline earth metal hypohalites are used.

The use of sodium hypochlorite as an oxidizing agent is also advantageous for the following reason: In making indigo the mixed sodium and potassium hydroxide used in the caustic fusion is recovered and returned to the system for further use. However, the ratio of sodium hydroxide to potassium hydroxide must be substantially constant for the caustic fusion, and since sodium amide is added during the fusion this causes the proportion of sodium in the recovered caustic to be greater than desired. Consequently, carbon dioxide is blown into the mixture to remove the excess sodium as sodium carbonate, this being made possible by the greater ease with which sodium is carbonated in preference to potassium. This sodium carbonate is removed from the caustic mixture by filtration. Now when sodium hypochlorite is used as an oxidizing agent one of the products is sodium chloride which is removed without additional steps with the sodium carbonate, the resulting mixture of sodium carbonate and sodium chloride being capable of commercial use without separation or purification. This is a tremendous advantage and permits the production of my superior product without a corresponding increase in the cost.

This invention may be more readily understood by reference to the following illustrative examples, in which the quantities are stated in parts by weight.

Example 1

The alkaline melt of an indigo fusion, resulting from the fusion of 1350 parts of mixed sodium and potassium phenyl glycine, 627 parts of sodium amide, and 2200 parts of mixed potassium and sodium hydroxide at 225° C., was dissolved in water to give a 2% solution of alkali metal indoxyl (see U. S. P. 680, 395, Aug. 13, 1901 of

Phleger Deutschs Gold-und-Silber Scheide Austalt vorm. Rossler in Frankfort A/M or D. R. P. 137,955 and Anmeldung D 11.810 Friedlaender, "Fortschritle der Teerfarben Fabrikation" 6,568 of the same company). To 2500 parts of this solution were added 380 parts of a 10% solution of sodium hypochlorite. This was added as rapidly as possible following the course of the oxidation by spotting on porous paper, the oxidation being completed when the liquid flowing away from a spot of precipitated color does not become blue due to air oxidation of the soluble alkali indoxyl. Sodium hypochlorite was added until the greenish blue rim on the spot had disappeared. The indigo was filtered, washed free from inorganic impurities, and dried.

The product obtained was in a very fine state of subdivision, much finer than indigo which was obtained in the ordinary way by the air oxidation of alkaline leuco indigo or the alkali metal indoxyl. In the case of air oxidation it was precipitated as clusters of needles, while in the case of accelerated oxidation the crystals were so small that they were barely visible under high power magnification. This product, when ground in oil, gave a jet blue-black tone, while crystalline indigo obtained by air oxidation, applied in the same way, gave a flat brownish-blue tone of a decidedly lower covering power.

Example 2

To 2500 parts of a 2% alkali metal indoxyl solution, obtained from an indigo fusion as shown in Example 1, were added rapidly 285 parts of a 10% solution of sodium hypochlorite, this amount was insufficient to completely precipitate the indigo. The oxidation was then completed by blowing with air until a spot test showed a clear rim, indicating the complete oxidation of the alkaline indoxyl. The indigo which was filtered, washed and dried had properties somewhat similar to that obtained in Examples 1 and 2.

In place of sodium hypochlorite other alkali metal hypohalites, for example sodium hypobromite may be used with very satisfactory results. Due to the ready availability of sodium hypochlorite I prefer to use this oxidizing agent in carrying out the process of the present invention, although it is understood that any of the hypohalites described herein may be used without departing from the scope of the present invention.

The rate at which these agents are added may be varied within wide limits, from practically instantaneous addition to a rate comparable with air oxidation, without detracting from the superiority of the product.

The temperature at which the oxidation is carried out may be varied within rather wide limits also, say 0–80° C., atlhough it is advisable to carry out this oxidation in the neighborhood of 25° C. or lower, since the yield is thereby improved. By oxidizing within the relatively low temperature range of 0–25° C. over-oxidation to isatin as well as production of indirubine by-product is practically eliminated.

The strength of the hypohalite is susceptible of considerable modification but in general it may be stated that a dilute solution is preferable, since local over-oxidation is thereby undesirably decreased. The strength of the caustic solution in which the alkaline indoxyl is exposed is also susceptible of variation within a considerable range (roughly 10–25%) but somewhat better results are obtained by selecting a caustic solution having a strength within the range of about 15–17%.

An excess of hypohalite is very undesirable since it results in over-oxidation of the indigo to isatin. In order to avoid such over-oxidation of the indigo I prefer to add an amount of hypohalite somewhat less than sufficient to completely oxidize the alkaline indoxyl, and subsequently complete the oxidation by the use of air. The product produced thereby is much superior to the synthetic indigo heretofore used, and is almost as satisfactory as the product produced by completely oxidizing with a hypohalite. In this connection it may be stated that exceptionally satisfactory results can be obtained by oxidizing about 75% of the alkaline indoxyl with the hypohalite and completing the oxidation of the remaining 25% by means of air. However, it is to be understood that I do not intend to limit myself to a minimum oxidation of 75% by means of the hypohalites disclosed herein, since I have found that this accelerated oxidation may be dropped to a figure as low as 25%, the remaining 75% being oxidized by means of air, without losing all the advantages of the herein described process.

The products described herein have a wide variety of uses, particularly in the manufacture of pigments where a finely divided compound having excellent covering power is essential. These products are exceptionally well adapted for use in pigments for lacquers, rubber, printing inks, etc. In addition they may be used for any of the numerous purposes for which ordinary indigo is used, although their superiority over ordinary indigo is most pronounced when they are used in pigments.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for producing indigo having properties greatly superior to ordinary synthetic indigo which comprises subjecting alkali metal indoxyls to partial oxidation by means of alkali metal hypohalites, and completing the oxidation by means of air.

2. A process for producing indigo having properties greatly superior to ordinary synthetic indigo which comprises subjecting alkali metal indoxyls to partial oxidation by means of sodium hypochlorite, and completing the oxidation by means of air.

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