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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

Synthesis of 3,3'-dichlorbenzidine hydrochloride

Period Covered: March-June, 1944

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Progress Report

Title: Synthesis of 3,3'-dichlorbenzidine hydrochloride

Period Covered: March-June, 1944

SUBMITTED BY: O. H. Cooper DATE SUBMITTED: 7-10-44

APPROVED BY: A. M. Erskine 7/15/44 DATE ISSUED: 7-15-44

INTRODUCTION:

The limited availability of 3,3'-dichlorbenzidine led to a short investigation of the synthesis of this intermediate from ortho-nitro-chlor-benzene. It was known that other pigment manufacturers had already begun to synthesize their own intermediates, since Orchem was unable to produce more than was required for their own need in the manufacture of "Lithosol" Yellow G Concentrated. The purpose of this investigation was to gather sufficient information to determine whether we should undertake the manufacture of 3,3'-dichlorbenzidine at Newark.

SUMMARY & CONCLUSIONS:

The most common commercial practice for the synthesis of 3,3'-dichlorbenzidine from ortho-nitro-chlor-benzene involves a reduction of the nitro compound with zinc dust in alkaline medium, and the hydrazo compound formed thereby is subsequently rearranged by the action of mineral acid. This reduction may be carried out in alcohol solution (Reference 1), but the one attempt made in this laboratory to follow this procedure met with very little success. A much more commonly used method requires solvent naphtha as the reaction medium (instead of the alcohol of the earlier method), the other steps in the synthesis being essentially the same as those of the original method. The naphtha process is currently used by Orchem (Reference 2), and the method of preparing benzidine from nitrobenzene by this process is described in considerable detail in the literature (Reference 3). The method giving the most promising results in the current laboratory study was based essentially on the benzidine process described in the literature.

The procedure as currently practiced at Orchem is rather complicated and requires special equipment not presently available at Newark. Among the features of the Dyeworks procedure which would necessitate significant capital expenditure if we were to undertake manufacture at Newark are:

1. An emulsion of the solvent naphtha with water is formed at one stage in the process and special handling and treatment are required to break this emulsion.

2. Since solvent naphtha has a relatively low boiling point, an efficient water-cooled condenser is necessary to prevent excessive losses of the solvent during the reduction and subsequent rearrangement.

3. A distillation apparatus is required for recovery and rectification of the naphtha.

4. Owing to the flammability of the solvent, special precautions to guard against fire hazards are necessary.

Some of the objectionable features of this procedure have been circumvented in the laboratory by substituting per-chlorethylene (manufactured by the Elchem Department) for the solvent naphtha. The advantages of this solvent over naphtha are:

1. It does not form a stable emulsion with water, and consequently no special precautions and treatment to break an emulsion are necessary.

2. Since the solvent has a relatively high boiling point a water-jacketed condenser is not necessary and an efficient air condenser would probably be adequate to minimize losses through vaporization during the reaction.

3. Since the solvent is not miscible with water it is readily recovered by simple gravity separation from the mother liquor. Rectification of the recovered solvent is not necessary to permit its reuse in a subsequent run.

4. This solvent is non-flammable, and consequently no fire hazard exists. However, efficient ventilation is necessary since the vapors thereof are known to exert an undesirable physiological action.

Details of the laboratory process are described in the appendix. No extensive variable studies or yield studies were made. The objective of the current study was accomplished when it was shown that material satisfactory for use in our new Benzidine Yellow K-2008 could be made by this method.

As has already been indicated the only methods successfully applied in the laboratory for the synthesis were those using either solvent naphtha or per-chlorethylene as the solvent medium. Modifications, which met with little or no success that were studied included the following:

1. Use of alcohol as the medium.
2. Use of 50% alcohol.
3. Use of water with Duponol WA as the dispersing agent.

It was clearly shown in this study that adequate washing of the intermediate with water or an aqueous saline solution is necessary to assure a product of satisfactory quality. An impurity which is water soluble is formed in the dichlor-benzidine hydrochloride, and if this is not removed its presence is detected in the K-2008 pigment prepared therefrom by the following characteristics:

Masstone - light
Tint - weak and green
Oil Bleed - markedly inferior
Lightfastness - slightly inferior

It is quite likely that the inadequacies of insufficiently washed intermediates are due to the presence of ortho-chlor-aniline hydrochloride as an impurity. The likelihood of this possibility was demonstrated by adding known amounts of ortho-chlor-aniline to satisfactory dichlorbenzidine and obtaining the same deviations in tinctorial and fastness properties from standard K-2008 as was obtained by inadequately washed intermediates.

APPENDIX

SYNTHESIS OF 3,3' -DICHLORBENZIDINE HYDROCHLORIDE

112 grams ortho-nitro-chlor-benzene
500 cc per-chlor-ethylene
7.2 g. caustic soda 100% (as 50% aqueous sol.)
15 cc water

Stir and heat to 85-90°C on a water bath.

(Add intermittently in small portions)

152 grams zinc dust (reagent quality)

Maintain temperature at 85-90°C until reaction is complete. Endpoint: color changes from deep red to straw color.

Filter the hot reaction mixture and pour the filtrate with good stirring into

112 grams hydrochloric acid 100% (310 cc of 0.362 grams per cc)

Heat to 40-50°C. on a steam bath and continue stirring for 2-3 hours. Cool, filter, wash with small portions of per-chlorethylene and with successive portions of water or aqueous saline.

Average Yield (based on nitrite value) = 65-70% of theory.
Average Recovery of crude per-chlorethylene = 70-75%.

EXPERIMENTAL DETAILS

Notebook #1095. Expts. 1-16 inclusive.

REFERENCES:

1. P. Cohn - Ber. 33, 3552 (1900)

2. Letter A. Siegel to E. R. Allen (June 27, 1944)
Subject: "Dyeworks 3,3'-dichlorbenzidine process and equipment".
Report of visit to Dyeworks of March 16, 1944.

3. H. E. Fierz-David and L. Blangey
Farbenchemie 4th Ed. (1938) pp. 81-2 (Julius Springer, Vienna).