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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

Progress Report

SYNTHESIS OF INTERMEDIATES BY SULFURIC ACID BAKING PARA-TOLUIDINE-META-SULFONIC ACID AND PARA-CHLOR-ANILINE-ORTHO-SULFONIC ACID.

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INTRODUCTION:

The well known sulfanilic acid rearrangement (i.e. the synthesis of aniline-para-sulfonic acid from aniline by sulfuric acid baking) is used commercially to prepare several intermediates of importance to the lake industry. Among these are para-toluidine-meta-sulfonic acid ("Lithosol" Rubine BG intermediate) and para-chloraniline-ortho-sulfonic acid ("Lithosol" Scarlet 2YL intermediate). The former is synthesized from para-toluidine; the latter from para-chlor-aniline.

The comparative simplicity of these manufacturing processes has led to the consideration of their possible introduction at Newark. As a preliminary it was necessary to obtain some information on the laboratory preparations, which study constitutes the subject of the present report.

SUMMARY AND CONCLUSIONS:

It has been shown that both para-toluidine-meta-sulfonic acid (PTMSA) and para-chloraniline-ortho-sulfonic acid (PCAOSA) can be readily prepared in good yield by a sulfuric acid baking synthesis. Although only a limited amount of laboratory study was devoted to these preparations, nevertheless the yields obtained were quite encouraging. For PTMSA a maximum yield of 86.5% of theory was realized; for PCAOSA a yield of 70.5% was attained. It is reasonable to expect that a limited variable study, including investigation of the baking temperature and the duration of baking, may disclose conditions leading to still higher yields. No further laboratory study of these specific syntheses is contemplated at the present time.

Any equipment installation suitable for the manufacture of PTMSA would also be suitable for the preparation of other intermediates by the sulfuric acid baking synthesis. At the present time the two intermediates covered in this report and "Lithosol" Red 2B Acid are the only ones synthesized by this method which are currently used at Newark. However, it is possible to prepare many other products, some of which are definitely speculative and the merit of which has yet to be demonstrated, and it is planned to high spot such possibilities. For this purpose cheap substituted aniline compounds, which on theoretical grounds should lend themselves to conversion by the sulfanilic acid type of rearrangement, are being investigated. This speculative study will be reported elsewhere.

GENERAL DISCUSSION:

The preparation of PTMSA from para-toluidine by treatment with concentrated sulfuric acid and subsequent baking is frequently mentioned in the early literature (Ref. 1), but the directions for the preparation are none too explicit. Two attempts to prepare PTMSA in accordance with these vague directions led to only limited success, the maximum yield obtained being 39.4% of theory.

A very careful investigation of the conditions necessary to assure maximum yields in this baking process was made by Huber (Ref. 2). By following the recommendations of Huber it was found possible to increase yields significantly to 86.5% in the case of PTMSA. In Huber's work it was clearly demonstrated that two stages of the preparation are critical in determining yields; these are:

1. The formation of the acid sulfate from the free base.

2. The baking of the acid sulfate to effect the rearrangement to the amine sulfonic acid.

In the early literature it was apparently common practice to form the acid sulfate by treatment of the amine with concentrated sulfuric acid. As is well known, it is extremely difficult to obtain a uniform reaction by such a procedure. Huber recognized that the nonuniformity of this treatment led to complications, such as formation of disulfonic acids and other by-products, in the subsequent baking stage of the synthesis. However, by using diluted sulfuric acid - Huber recommends 70% in most cases - it is possible to prepare the amine acid sulfate in aqueous solution at high temperature. Even though this crystallizes on cooling, nevertheless a uniform product has been assured by its preparation in solution.

Since for every mole of amine acid sulfate rearranged to the amine sulfonic acid, one mole of water is liberated, and since this reaction is reversible, Huber recognized the value of working at reduced pressure during the baking. For similar reasons the duration of the baking cycle may be reduced when operating at reduced pressure.

In all cases but one, the PTMSA and PCAOSA made in the laboratory were purified by extraction with aqueous caustic soda and subsequent precipitation by acidification. In this manner little trouble was encountered in removing the hard reaction mass from the baking process. In the one case where an attempt was made to obtain the PTMSA in crude form (i.e. as obtained directly from the baking process), considerable trouble was encountered in removing the hard reaction mass from the enamel pan in which the baking had been conducted. In this case considerable mechanical force, such as hammering of the bottom of the enamel pan, was necessary. It is obvious that the removal of the crude intermediate constitutes a problem for serious consideration by competent engineers in the event that we should decide to manufacture the intermediate and retain it in crude form.

Another possibility is to extract the intermediate with aqueous caustic soda and to retain it as a stock solution of the sodium salt pending consumption in regular manufacture of Rubine BG pigment. A piece of clean degreased wrought iron immersed in such a

solution for 82 days showed a gain in weight of only 0.06%. At the end of this period the appearance of the iron was satisfactory, evidence of corrosion appearing only at the freshly cut surfaces. It is therefore safe to assume that a storage tank made of wrought iron would be satisfactory for retention of a stock solution of the sodium salt of PTMSA.

Purified laboratory PTMSA and the sodium salt stock solution were found to be satisfactory for the manufacture of "Duol" Carmine (RT-443-D) by the K1994 (direct laking) process or suitable modifications thereof. The one laboratory preparation of crude PTMSA (nitrite value 65.7%) did not give satisfactory results in this process. However, it seems reasonable to assume that had suitable pH adjustments been made at the crucial points, the crude intermediate could have been made to work satisfactorily.

The PCAOSA (Scarlet 2YL intermediate) gave emminently satisfactory Watchung Red BX, RT-488-D, by laboratory raw material tests.

APPENDIX

PREPARATION OF PTMSA

196 grams Sulfuric Acid (111 cc. of conc.acid, 96%, sp.gr. = 1.84)	Add to
75 cc water	with stirring. Heat to 100-110°C. Add gradually with stirring during 40 minutes
214 grams para-toluidine	Stir 5 minutes after addition is complete. Pour the solution of para-toluidine acid sulfate into a round-bottom flask. Heat on oil bath at 210-230°C. for 4 hrs. at a pressure of 50-90 millimeters of mercury. Cool and extract with
200 grams caustic soda	dissolved in
1000 cc. of water	at the boil. Use additional
1000 cc. of water	for washing.
	Steam distill until the distillate is no longer cloudy. Boil the solution remaining in the distillation flask with
10 grams Norite 10 grams Filtercel	for 15 minutes. Filter through steam-jacketed Buchner funnels. Add with stirring
176 grams sulfuric acid, 100% (as a 50% solution)	
	A fine cream-colored precipitate is obtained.
	Filter, wash, and dry at 140°F.

PARA-CHLOR-ANILINE-ORTHO-SULFONIC-ACID

Preparation of PCAOSA is very similar to the foregoing preparation of PTMSA. However, because of the lower solubility of the acid sulfate of para-chlor-aniline, suitable modifications in the solution stage must be made. In addition definite evidence was obtained that longer baking is necessary, 10 hours at 210-230°C. being required to attain a yield of 70.5%.

EXPERIMENTAL DETAILS:

PTMSA Synthesis

Notebook 1102, Expts. 1 to 6 incl.

PCAOSA Synthesis

Notebook 1102, Expts. 7 & 8.

PTMSA - RM Tests

Notebook 1098, Expts. 18 & 25.

PCAOSA - RM Tests

Notebook 986, Expts. 34 & 35.

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1. Neville, Winther - Ber. 13, 1947 (1880)
Richter - Ann. 230, 314 (1885)
Wynne, Bruce - J. Chem. Soc. 73, 738 (1898)

2. Huber - Helv. Chim. Acta 15, 1372-83 (1932)