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PREPARATION AND CONSTITUTION OF A SYNTAN BASED ON PARA TERTIARY BUTYLPHENOLIC NOVOLAC

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Preparation of the sulphonated p-tertiary butylphenolic novolac and its constitution has been reported.

In an earlier publication¹ the synthesis and the constitution of para tertiary butylphenolic novolac was reported. The present paper deals with the sulphonation of the novolac, the constitution of the sulphonated novolac and its use as a potential synthetic tanning agent for leather manufacture.

Experimental

Two dimensional paper chromatographic studies were conducted on Whatman chromatographic paper (Grade 3 MM) using the solvent system:

(a) Methanol — water (7:3 V/V) in the first direction followed by (b) methanol — water — chloroform (2:1:1 V/V) in the second direction for novolac. For the sulphonated novolac, chromatography was carried out using the solvent system (c) 6% acetic acid in the first way followed by (d) n-butanol — acetic acid — water (4:1:5 V/V)² in the second way. The chromatograms were developed with (i) 0.3% ferric chloride solution and (ii) a mixture of 0.3% ferric chloride and 0.3% potassium ferricyanide solution. Infrared spectra of the com-

pounds were taken using Perkin Elmer I. R. spectrophotometer model 337.

Preparation of sulphonated novolac

To the novolac melt prepared as described previously (50 g.) Conc. sulphuric acid (A.R, 25 g.) was added during ten minutes with constant stirring and the contents were heated on a water bath for three hours at 85°C. Then the temperature was raised to 90°C and the heating continued for two more hours at that temperature. After five hours, sulphonated product was tested for its solubility. It did not give a clear solution and so the heating was continued for one more hour to complete sulphonation. After six hours, the product was completely soluble in water to a clear solution.

Purification of the sulphonated novolac

The sulphonated novolac was then freed from small amount of unreacted novolac and the unreacted sulphuric acid following the procedures of Strachota³ and Huff *et al.*⁴ respectively, are described below in brief.

The sulphonated novolac (10 g.) was dissolved in distilled water (25 ml.) and extracted with ether* in a liquid-liquid extractor to remove free novolac (1.35%). The residue was treated with saturated barium hydroxide solution in excess and heated on a water bath for one hour. The precipitated barium sulphate was filtered and washed with a small quantity of water. The filtrate along with the washings was passed through Dowex 50W - X8 (sphericity 85%) H⁺ resin column. The eluent was then evaporated to dryness *in vacuo* to give sulphonic acid as semi solid (4.5 g.).

Estimation of sulphonic acid in the sulphonated novolac

The total number of sulphonic acid groups present in the sulphonated novolac was estimated by the non-aqueous titration technique of Nayudamma.*

a) Preparation of the mixed solvent

The mixed solvent was prepared using glycol, η -butanol and benzene in the ratio 2 : 1.5 : 2

b) Preparation of standard alkali solution

Standard sodium hydroxide solution (0.1 N) was prepared in the mixed solvent in the usual way.*

c) Procedure

The sample (0.2 - 0.3 g.) in the mixed solvent (55 ml.) was titrated against 0.1 N standard sodium hydroxide solution using Beckman pH meter and the contents were thoroughly stirred by a magnetic stirrer. A blank was always carried out for the same amount of the mixed solvent (55 ml.) The percentage of sulphonic and sulphuric acids were then calculated in the usual way (1 ml. of 0.1 N sodium-hydroxide corresponds to 0.0081 g. sulphonic acid - SO₃H).

*II. Oxidation method using perchloric and nitric acids mixture**

The sample (500 mg) in distilled water (25 ml.) was treated slowly with a mixture of nitric acid (6 ml.) and perchloric acid (2.5 ml.) in a Kjeldal flask and left overnight. It was then heated on a water bath (15 minutes) and then heated directly on a gas flame until the solution become colourless. After cooling down to the room temperature, conc. hydrochloric acid (2.5 ml) was added and was heated (5 minutes). This was then cooled, diluted with water (100 ml.) and analysed gravimetrically for sulphate by precipitation with barium chloride solution in the usual way.

*III. Potentiometric titration method**

The sample (500 mg.) in distilled water (20 ml.) was titrated potentiometrically with 0.1 N standard aqueous sodium hydroxide solution to pH 5.5. The sulphonic acid content was then calculated in the usual way.

Tannin studies of the Sulphonated novolac

The syntan was analysed for tannin and non-tannin content and the data are given in Table I.

The tanning properties of the syntan were tested. One goat skin was processed upto pickle stage in the usual manner. For the pelt, (100 g.) in water (100 ml) was added initially the syntan (2 g.) and shaken for half-an-hour. Then the syntan amount was gradually increased upto 12 g. during the course of 3 hours. At the end of the period, the pelt was tested for its shrinkage temperature and pH. The shrinkage temperature was 72°C and the pH of the pelt and the bath was 2.4.

Discussion

The preparation of syntans in general is mostly confined to the patent literature. Literature survey has revealed that there is not much development on the constitutional aspects of syntans. Reich *et al*⁵ have brought out some publications on the constitution of naphthalene based syntans and sulfone based syntan. Croad⁷ and later Kuntzel and Schwank⁸ had established the tanning properties of sulphonated novolacs. Ekstrom⁹ showed that the size of the novolac beyond a particular limit was not very important for having tanning potency. He pointed out that the position of the hydroxyl and sulphonic acid groups in the molecule were important factors for its tanning potency which conclusion was later confirmed by Tu and Lollar¹⁰ and Otto.¹¹ Strachota¹² studied the unsulphonated novolac for its molecular weight and other properties. Tishchenko and Uvarov¹³ prepared syntans based on known cresol-formaldehyde novolacs and observed that the sulphonated novolac contained only one sulphonic acid group. They sulphonated the novolac (taken in acetic acid) at room temperature. Under that condition it formed only monosulphonic acid. But in contrast, in the present work even at high temperature (85-90°C) the paratertiary butylphenolic novolac gave on sulphonation only monosulphonic acid. However, paper chromatogram showed the presence of monosulphonic acid as the major spot associated with traces of other compounds. The non-aqueous titration studies and the oxidation experiments of the sulphonated product clearly showed that it was monosulphonated novolac. It was also confirmed by paper chromatographic studies of the purified compound which showed essentially a single spot. Rf values of novolac in (a) and in (b) were 0.73 and 0.64 respectively. Rf values of sulphonated novolac in (c) and

(d) were 0.59 and 0.72 respectively. (Figs. 1 and 2)

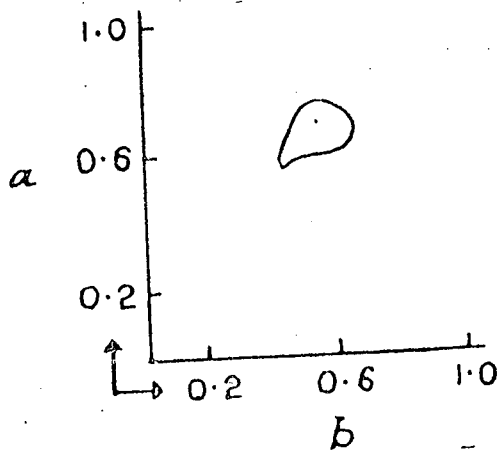


Fig. 1

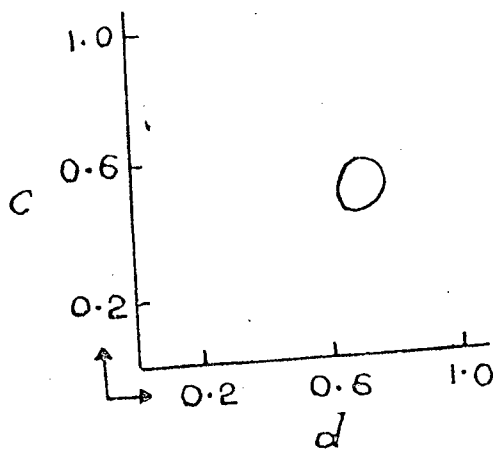


Fig. 2

Colour reactions of novolac and sulphonated novolac on paper chromatographic spots in the visual and ultra-violet light are given in Table 2

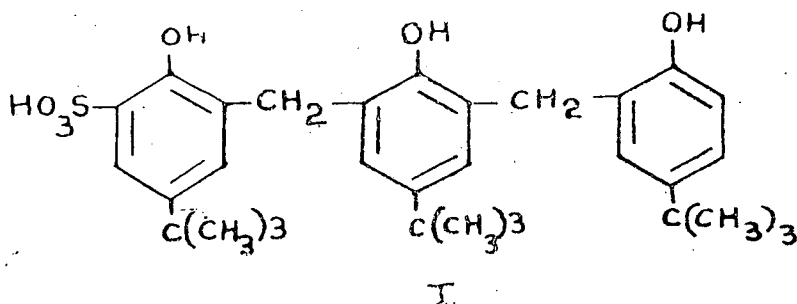
TABLE 1

<i>pH of the syntan</i>	<i>% Tannins</i>	<i>% Non-tannins</i>	<i>% Total solids</i>	<i>% Insolubles</i>	<i>% Moisture</i>
2.4	48.22	16.85	84.55	19.48	15.45

TABLE 2

	<i>VISIBLE</i>					<i>ULTRA VIOLET</i>						
	<i>Ammonia solution</i>	<i>Ferric chloride solution</i>	<i>Ferric chloride + potassium ferricyanide solution</i>	<i>Bisdiazotised benzidine</i>	<i>Pine Krypton Yellow</i>	<i>Ammonia solution</i>	<i>Ferric chloride solution</i>	<i>Ferric chloride + potassium ferricyanide solution</i>	<i>Bisdiazotised benzidine</i>	<i>Pine Krypton Yellow</i>		
Novolac I	Colourless	Colourless	Yellowish green	Bluish dark	Yellow	Greenish yellow	Pink	Reddish Pink	Greenish yellow	Violet	Yellowish brown	Bluish green
Sulphonated Novolac II	Reddish brown	Slight red	Bluish Yellow	Bluish dark	Yellow	Greenish yellow	Violet	Blue	Greyish yellow	Violet	Greyish yellow	Bluish green.

The attachment of the sulphonic acid group was considered at the ortho position with respect to the phenolic group of the first ring of the trimer (I) since the para positions are already blocked by the tertiary butyl groups.



Despite the amount of sulphuric acid taken in excess for the sulphonation resulted in the formation of mono-sulphonic acid only. The unreacted sulphuric acid was not interfering in any way in the subsequent operations of tanning.

The syntan shows promising results to be used as a pretanning syntan. This also can be used as an ancillary tannin along with vegetable tanning materials to increase its penetration and final yield of the leather.

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