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A New Process for the Synthesis of Naphthalene Based Tanning Agent

Sarwat Jahan Mahboob*, Muhammad Ishaq Subhopoto, Rajkumar Dewani, Muhammad Kashif Pervez and Farrukh Nazir

PCSIR Leather Research Center, D/102, South Avenue, S.I.T.E, Karachi-75700, Pakistan

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Abstract. A new process developed for the preparation of naphthalene catechu tanning agent consisted of sulphonation of naphthalene, condensation with formaldehyde, combining with naturally occurring catechol, followed by neutralization of the reaction mixture. The product was then dried, analyzed and tested for application on wet blue leather which showed excellent tanning properties.

Keywords: syntan, catechu, naphthalene, tanning agent

Introduction

Different aromatic substances i.e., phenol, cresol and naphthalene have been treated with formaldehyde in presence of sulphuric acid and sodium hydroxide as catalyst to form polymeric substances that may be used as syntan (Romaniv and Berkman, 1970; Berkman *et al*., 1968). The synthesis was based on three main steps comprising of sulphonation, condensation and neutralization. Naphthalene after sulphonation forms naphthalene sulphonic acid (Berkman and Sergeeva, 1957), which then condenses with formaldehyde to form water soluble acid naphthalene syntan which may be marketed as an acid liquid for whitening chrome leathers or bleaching vegetable tannins. It may also be neutralized to form neutral salt of the syntan, which after drying may be marketed as solid syntan (Thorstensen, 1993). Naphthalene based syntan has remarkable properties as a tanning agent but its light fastness is not as good as other synthetic tanning agents (Palop *et al*., 2008) which are biodegradable as well (Danhong *et al*., 2008). Studies have been reported for effects of naphthalene syntan with vegetable tannins (Dalen, 2003). Addition of naphthalene sulphonic acid to other tannins has been found to be advantageous and white spots on vegetable tanned leather disappear when it is used in the tanning mixture (Alois, 1964). In order to enhance the tanning properties, a new effort for preparing syntan was carried out with locally available catechol based tanning material, called catechu. The resulting product showed excellent tanning characteristic with less environmental hazards. It could be economical and feasible commercial level (Covington and Song, 2003; Shuttleworth, 1952).

*Author for correspondence; E-mail: sarwatjmahboob@hotmail.com

Materials and Methods

The chemicals used in the synthesis were conc. sulphuric acid, specific gravity 1.84%, obtained from BDH, formaldehyde 37%, obtained from Merck, sodium hydroxide commercial grade, obtained from Winlab while naphthalene and catechu were of commercial grade. Mechanical agitator was used for shaking the aqueous liquor. All steps of synthesis, retanning and analysis were carried out conventionally.

Official Method of Tannin Analysis of the Society of Leather Technologists and Chemists (Lampard, 1996) was used as reference in the analysis involving the steps as given below:

Sulphonation. Naphthalene (65.0 g) was melted in a closed reaction vessel fitted with electrical stirrer. Concentrated H_2SO_4 (84.65 g) was added over a period of approx., 10 min till the whole naphthalene melted. A pinch of catalyst, $ZnSO_4$ (commercial), was also added and stirring was continued for 2 h at 150-155 °C until reaction mixture became completely water soluble resulting in blackish grey highly viscous liquid.

Condensation with formaldehyde. Thereafter, formaldehyde (11.65 g) was added dropwise at a temperature of 40 °C during 10 min with further 2 h stirring on a water bath at 40 °C. Care was taken to control the temperature of the reaction mixture at 100 °C. Water soluble dark grey viscous liquid was obtained after completion of the reaction.

Blending with catechu. Water soluble and filtered form of catechu (65.0 g) was completely dissolved in minimum distilled water, and then added with constant stirring at room temperature till a homogenous liquid was obtained.

Neutralization. The mixture was then neutralized with soluble sodium hydroxide (35.0 g) with constant stirring until it

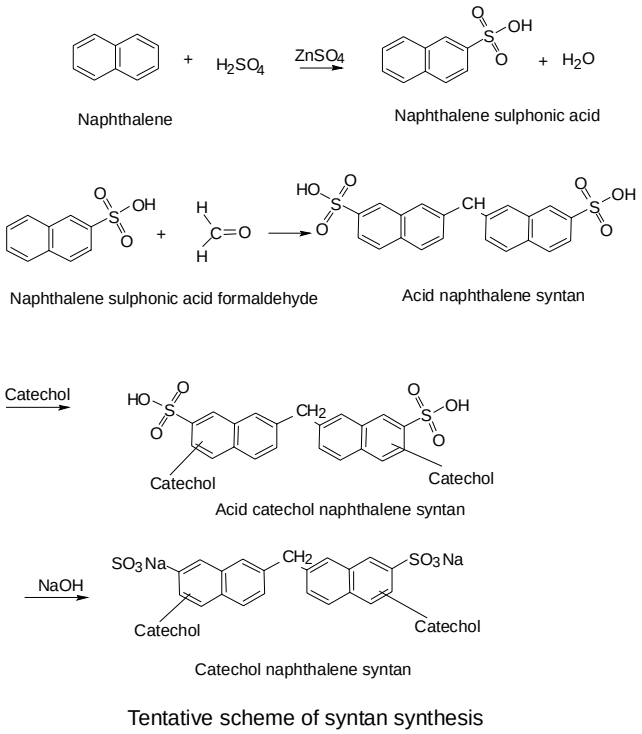
became completely water soluble, grayish brown liquid having pH 4.5 which after drying became brown solid at room temperature.

Application on leather. The process for retanning chrome tanned leather was carried out as follows:

Moisturized and shaved chrome tanned leather (100.0 g), having a shaved thickness of 1.5 mm was taken in a flask with 5% aqueous solution of the prepared syntan; pH was maintained at 6.0. It was then shaken on a mechanical shaker at 30 °C and flexibility, penetration was checked after every 30 min by cutting the leather at various sides. After 1.5 h shaking, 100% penetration in the leather was observed, which was then taken out and fat liquoring was performed in the usual manner.

Results and Discussion

Naphthalene reacted with conc. H_2SO_4 forming *â*-naphthalene sulphonic acid. Condensation with formaldehyde yielded acid naphthalene based syntan which when neutralized with sodium hydroxide gave a neutral salt of the same syntan (Dev *et al*., 1979). Some parameters, which are important in sulphonation, condensation polymerization, were given special attention including molar ratios of the reactants, temperature, time period, degree of hardness of the polymer, degree of neutralization and solubility of the polymer in various solvents. Mainly, four steps were performed during the chemical reaction, i.e., sulphonation, condensation, blending with catechu and neutralization. The last step determines water solubility of the polymer, which is the most important factor because such syntan should be soluble in water. This syntan is an example of a material capable of being absorbed by the hide protein through not only hydrogen bonding but also electrostatic attraction. Vegetable and synthetic tannins are high molecular weight compounds. Naphthalene part gets attracted to the receptive sites of collagen through H bondings and electrostatic attraction of multivalent anions enables them to simultaneously occupy positions adjacent to all the oppositely charged side-chain groups, while catechol tannins get attached to the collagen by multiple hydrogen bond cross linking; it influences the fixation to the collagen strongly (Shuttleworth, 1952). Naphthalene syntans do not have a significant effect on Cr (VI) formation but condensed with catechol tannins have very good reducing effect. When dissolved with vegetable tannin, it aids in dispersing the tannin particles and helps in the penetration in the hide and also brightens the colour (Thorstensen, 1993). Plant tannins can remain bound to the fiber and reduce Cr (VI) formation and provide anti-oxidant protection (Lu *et al*., 2003; Covington and Shi, 1998). During retanning, addition of any neutralizing agent was not required as naphthalene based syntan also acts as neutralizing agent for chrome tanned leather and also makes the fibers tight thus preventing the loss of the grain (Sarkar, 1991). So far, different analytical methods have been developed for the analysis of naphthalene based syntans (Lawrence, 1981; 1980; Sriram and Ramaswany, 1979). Laboratory tests of the prepared syntan were performed with reference to the Official Methods of Tannin Analysis of the Society of Leather Technologists and Chemists (Lampard, 1996). All the experiments were performed in duplicate and the average values are given in Table 1.



Tentative scheme of syntan synthesis

Table 1. Analysis of syntan

Name of test	Reference	Value (%)
Moisture	SLC 113	6.5
Total solids	SLC 114	93.4
Total solubles	SLC 115	93.3
Non-tannin constituents	SLC 116	16.07
Tannin matter absorbable by hide powder	SLC 117	77.3
Insolubles	SLC 118	0.03
pH of syntan solution	SLC 120	4.5

Conclusion

The synthesized syntan may be considered a green product being synthesized and applied for the first time. Moisture was determined by direct drying. Tannin infusion was not filtered as the solution was optically clear; kaolin was not used as it is required in filtration if the need arises (Lampard, 1996).

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