

SULPHUR DYES FROM BLACK LIQUOR

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Abstract. Black liquor, a waste product of paper mills, has been utilized for preparing dark brown sulphur dyes. The lignin obtained on acidification of black liquor was thionated both by liquid and dry methods under different conditions. Dye obtained by dry thionation under certain conditions was fast to washing and light. It was comparable in substantivity to sulphur brown. It had a Dygar strength of 115% as compared to commercial sulphur brown of 25%.

Sulphur dyes are prepared from a variety of raw material through a process called sulphurisation or thionation. The structure of the product obtained from the simplest starting material is so complex that it has not been established with any degree of certainty so far. The researches carried out by Gnehm and Kaufler,¹ Herz,² Fierz-David and his coworkers,³ and Zerweck and his coworkers⁴ have shown that some of the most important commercial sulphur dyes contain, as chromophores, ring structures of the thiazole, thiazone or thianthrene types.

The significant part of the total sulphur is attached to the aromatic ring in the form of disulphide or disulphoxide bridges. These linkages are converted in sodium sulphide vat to —SNa groups, which on air oxidation form the final sulphide *in situ*. In fact the reduction of sulphide group to hydrosulphide with sodium sulphide distinguishes this group of dyes from vat dyes which are reduced by hydrosulphite.

Sulphur black is the most important dye of this class. It is manufactured and consumed in quantity. In fact its tonnage is unexcelled by any other single dye. This is manufactured in Pakistan by Pak Dyes and Chemicals, Daudkhel, from imported nitrophenol.

The facts that these dyes can be made in simple equipment and are needed in quantity, prompted us into investigations for indigenous raw materials for this group of dyes. An attempt was made by Karimullah *et al.*,⁵ who prepared grey dye from 4-chloro-2-nitrophenol obtained from *p*-dichlorobenzene in DDT waste.

The most important criterion for success in this class of dyes is cheapness. We had limited our search to most abundantly available material. From this angle we had chosen to work on lignin from paper mill waste, which is available in large quantity practically free of cost.

The wood consists of about 25% lignin which has to be removed before converting into chemical pulp for paper making. In Karnaphuli Paper Mills alone 15,000 tons of lignin is separated from bamboo annually and this quantity is burnt to recover chemicals. Processes are available whereby lignin can be separated from the chemicals to be reused in the paper mill without burning it. Thus lignin can be available very cheaply and in a concentrated form from this source. Other paper mills, one at Charsadda and the other at Lahore, can provide lignin in less concentrated

form. As more mills are being set up, its disposal, in fact, is a problem. This should prove an ideal material for a few dyes of this group.

Lignin was tried for this purpose as early as 1901. Robson⁶ used waste sulphite liquor in combination with salts to produce grey black dyestuff which perhaps could not find its way to the market. Peculiar economics of our country, where aromatic raw material is conspicuous by its absence, prompted us to prepare dyestuff from lignin. However, waste sulphite liquor was not used as a starting material because its lignin content was too small to make its use economical. Black liquor being a very concentrated source, was used instead.

Results and Discussions

Black liquor from Karnaphuli Paper Mills was used in these experiments. Lignin can be separated from this liquor on mere acidification. Sulphides present in the liquor get decomposed and alkali neutralised. Lignin, being insoluble in acids, gets precipitated.

As lignin is known to take up nitrogen on treatment with HNO₃ under even ordinary conditions, therefore, to get additional chromophores black liquor was precipitated with HNO₃. The reddish brown product obtained by this treatment was used in the initial experiments.

Both aqueous thionation and bake method were employed. It was observed that increasing severity of the reaction conditions resulted in intenser shades. This is obvious from the Table 1 where intensity of shade of cloth dyed with dye prepared by different methods is recorded.

In view of the fact that only the bake method gave reasonably intense shades, efforts were centred to this method during the subsequent work.

The effect of time of baking on the intensity of shade is shown in Table 2.

The dye obtained under these conditions was not fast to washing. A comparison of the shades of washed and unwashed dyed samples of cloth is given in Table 3. These samples were dyed consecutively from the same bath.

It is observed that the take up of the dye initially was 50% and on subsequent third dyeing, it was reduced to 30%. This was also observed that the dye was not fast to washing.

TABLE 1. EFFECT OF CONDITION OF THIONATION ON SHADE OF DYE.

| Reaction conditions | Temp (°C) | Shade (Lovibond units) | | | |
|---------------------|-----------|------------------------|-----|-----|-------|
| | | R | Y | B | Total |
| Refluxing (3 hr) | 100 | 1.0 | 1.4 | 0.7 | 3.1 |
| Heating (1 hr) | 175 | 3.1 | 4.0 | 2.9 | 10.0 |
| Baking (1½ hr) | 200 | 4.1 | 6.0 | 4.3 | 14.4 |

TABLE 2. EFFECT OF TIME OF BAKING ON INTENSITY OF SHADE.

| Baking time (hr) | Shade (Lovibond units) | | | |
|------------------|------------------------|------|-----|-------|
| | R | Y | B | Total |
| 1½ | 4.1 | 6.0 | 4.3 | 14.4 |
| 4 | 4.8 | 6.3 | 5.3 | 16.4 |
| 10 | 7.0 | 11.0 | 9.7 | 27.7 |

TABLE 3. SHADES OF WASHED AND UNWASHED DYED CLOTH.

| Dye trial No. and description | Shade of cloth (Lovibond units) | | | |
|-------------------------------|---------------------------------|------|-----|-------|
| | R | Y | B | Total |
| I Unwashed | 7.0 | 11.0 | 9.7 | 27.7 |
| | 4.0 | 5.0 | 4.1 | 13.1 |
| II Unwashed | 7.0 | 10.0 | 8.0 | 25.0 |
| | 3.3 | 4.0 | 3.0 | 10.3 |
| III Unwashed | 6.0 | 8.6 | 6.5 | 21.1 |
| | 2.2 | 2.4 | 2.2 | 6.8 |

The experiments performed with the lignin separated with HNO₃ were not very promising. The assumption that the presence of nitrogen in lignin would help in intensifying the shade did not prove correct. Moreover, HNO₃ oxidized lignin, reduced its yield and made reaction mixture more sticky and difficult to stir. Moreover, the product was not fast to washing.

The overall improvement resulted when HCl was substituted for HNO₃. The dyestuff prepared from lignin separated with HCl under the same conditions of reaction was found to be comparatively intense in shade and fast to washing.

A typical preparation required 6 hr baking giving a product of 85% solubility in water. Cotton cloth dyed with this dye was fast to washing and light. Table 4 and Fig. 1 show the shade of the cloth dyed at different concentrations of dye under identical conditions.

The concentration is expressed in terms of percentage of dyestuff on the weight of cloth dyed per 10 ml of the solution.

The shade of the dye at the above concentration has been interpreted in Table 5.

It is clear from this table that though the intensity of shade increases with the increase in the concentration of the dyebath, yet the shade tends from yellowish brown to bluish brown as concentration goes up. Fig. 1 also indicates that 1% of the concentration of the dyebath would suffice for all

TABLE 4. EFFECT OF CONCENTRATION OF DYEBATH ON THE INTENSITY OF SHADE.

| Dyebath concn (%) | Shade of cloth (Lovibond units) | | | |
|-------------------|---------------------------------|-----|-----|-------|
| | R | Y | B | Total |
| 0.25 | 3.7 | 5.5 | 4.6 | 13.8 |
| 0.50 | 4.6 | 6.5 | 5.6 | 16.7 |
| 1.0 | 5.6 | 8.3 | 7.4 | 21.3 |
| 2.0 | 5.6 | 8.3 | 7.6 | 21.5 |
| 3.0 | 5.7 | 8.3 | 8.1 | 22.1 |
| 4.0 | 5.8 | 8.5 | 8.3 | 22.6 |
| 5.0 | 5.9 | 8.4 | 8.5 | 22.7 |
| 6.0 | 6.1 | 8.6 | 9.0 | 23.7 |

TABLE 5. INTERPRETATION OF SHADES OBTAINED WITH DIFFERENT CONCENTRATION.

| Concn (%) | Interpretation | | | |
|-----------|----------------|-------|--------|------|
| | Neutral | Green | Yellow | Blue |
| 0.25 | 3.7 | 0.9 | 0.9 | 0 |
| 0.50 | 4.6 | 1.0 | 0.9 | 0 |
| 1.0 | 5.6 | 1.8 | 0.9 | 0 |
| 2.0 | 5.6 | 2.0 | 0.7 | 0 |
| 3.0 | 5.7 | 2.4 | 0.2 | 0 |
| 4.0 | 5.8 | 2.5 | 0.2 | 0 |
| 5.0 | 5.9 | 2.5 | 0 | 0.1 |
| 6.0 | 6.1 | 2.5 | 0 | 0.4 |

TABLE 6. RATE OF EXHAUSTION OF DYEBATH.

| Reading taken after | Dyebath concn (%) | | | |
|---------------------|-------------------|---------------|--------------------|--------------------|
| | Lignin (6%) | Lignin (1.5%) | Sulphur black (6%) | Sulphur brown (6%) |
| First dyeing | 71 | 61 | 11 | 59 |
| Second dyeing | 53 | 33 | 7 | 33 |
| Third dyeing | 36 | 16 | 4 | 23 |
| Fourth dyeing | 26 | 5 | — | 20 |

practical dyeing as intensity of the shade on the cloth does not increase very much with further increase in concentration.

Substantivity. The exhaustion properties of the dyebath were studied in comparison with sulphur black and sulphur brown. Comparison was made in 6% bath for each dye by dyeing equal weights of cloth consecutively and estimating the concentration of dye in the bath colorimetrically. Studies were also made at 1.5% concentration of the experimental dye to equalise its concentration with sulphur brown on Dygar standard. The observations are recorded in Table 6 (Fig. 2).

It is evident that exhaustion in the case of sulphur black is very sharp. Practically all the colour is taken up by the cloth in the first dyeing. The dye, however, compares very well with sulphur brown. In fact its substantivity is somewhat better.

Colour Strength. The colour strength of a dyestuff may be measured in terms of Dygar value proposed by Garner.⁸ For comparison two well-known dyes of the same class, that is sulphur black and sulphur brown, were selected. Reading the concentrations of dyebaths at a point where the intensity of shade

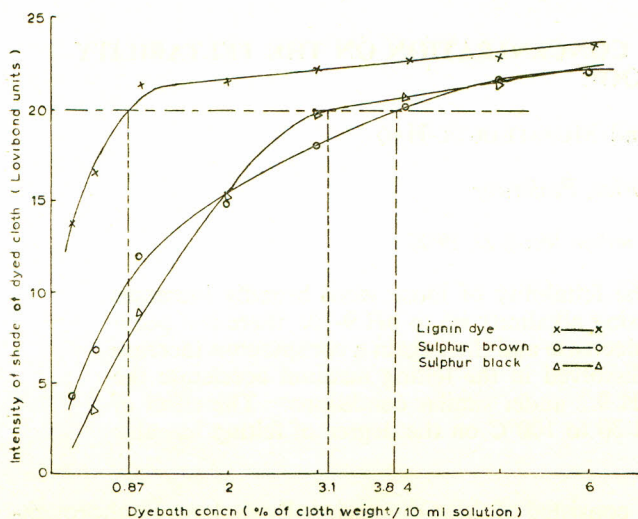


Fig. 1. Colour strength of dyestuffs.

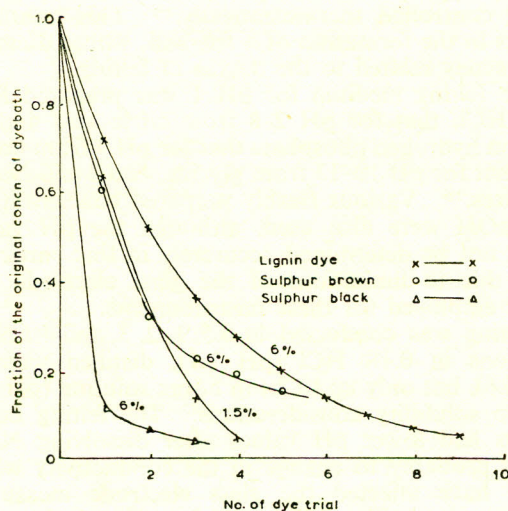


Fig. 2. Exhaustion of dye bath.

equals 20 units, the comparative strength of the dye from Fig. 1 works out as under:

| | |
|---------------|------------|
| Sulphur brown | 25% Dygar |
| Sulphur black | 30% Dygar |
| Lignin dye | 115% Dygar |

Hence the dye as such is about four times stronger than the commercial products.

Experimental

Precipitation of Lignin. Concentrated black liquor from the Karnaphuli Paper Mills was taken in a trough. HCl (concd) was added in piecemeals with continuous stirring. It was necessary to withhold

further addition of the acid to suppress foaming developed with the evolution of H_2S . When the liquor was completely neutralized, the addition of acid was stopped. 10 ml HCl (concd) was necessary for each 3.25 g separated dry lignin.

Preparation of Lignin Dye. Twenty grams each of Na_2S and S were taken in a beaker and heated on a sand-bath. Intense red coloration of polysulphide developed within a few minutes. Twenty grams of separated dry lignin was added and the contents were continuously stirred to prevent local heating. The temperature was raised to $200^\circ C$ and heating continued for 6 hr. The dye was cooled and stored (yield, 34 g; solubility in Na_2S , 85%).

This dye was used as such for normal dye trials. When a pure dye was required the raw dye was dissolved in Na_2S , filtered, acidified (H_2SO_4) again filtered and the precipitate washed, dried.

Procedure for Dyeing. Dye (0.5 g) and Na_2S (0.7 g) were taken in a beaker and solution was made to 100 ml in water. It was heated to about $70^\circ C$. 5 g white long cloth piece was wet in water, squeezed and dipped in the dye bath. The temperature was raised until the solution was about to boil. After a few minutes 0.3 g NaCl was added and dyeing continued for 2 hr. The cloth was continuously stirred for even dyeing. It was then removed from the bath and rinsed in tap water to wash away loosely absorbed dye. The dried cloth piece was studied for various tests.

Measure of Colour Strength. A range of dyeings with the dyestuffs at various percentages were dyed on cotton, using the normal dyeing method. The depth of each dyeing was measured on the Lovibond tintometer in terms of red, yellow and blue units. The units for each separate dyeing were totalled and plotted on graph. The points corresponding to a total of 20 units were noted. Colour strength of each dye was determined on the basis that 1% dyeing giving 20 units corresponds to 100% Dygar.

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