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STUDIES ON THE REACTION OF THE METAL-EXCHANGE PROCESS DURING THE PREPARATION OF LITHOL RED R (CI PIGMENT RED 49)

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SUMMARY

The degree of conversion of the sodium salt to the barium salt during the preparation of Lithol Red R (CI Pigment Red 49) was estimated by the colorimetric method. The conversion values obtained for different samples of sodium salt were checked against some model equations derived for solid state reactions.

The results suggest that after 5–10 min the reaction continues by a process of ion replacement in the crystal lattice.

The same method has also been applied to the study of the influence of rosin soap on the metal-exchange process. It was observed that addition of rosin soap yields both an increased conversion and an increase in the conversion rate probably due to the increased solubility of the dye by micellization.

1. INTRODUCTION

The most common method of production of toners is the conversion of sodium or ammonium salts of acid dyes to their less soluble barium, calcium or strontium salts. In some cases sodium salts are sufficiently insoluble for commercial application as cheap pigments for printing inks. In practice the metal-exchange or metallisation processes are achieved by heating a sodium salt of acid dye with the equivalent amount of barium or calcium chloride usually in an alkaline medium and in the presence of non-ionic surfactants.

It has been observed in commercial practice that the properties of the sodium salt of the dye, its crystal structure, morphology, particle size and other

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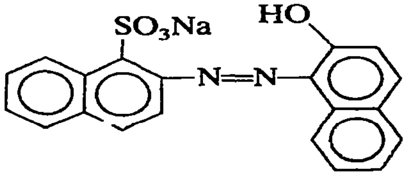
factors have a definite influence on the properties of the toners. Very often both the diazotization and coupling processes during dye synthesis determine the final result and the properties of the barium or calcium toners.

The purpose of this research was to carry out a more detailed study on the reaction of the metal-exchange process and to attempt to explain whether this reaction occurs by a solution mechanism or is the result of ion diffusion in crystals. The answer to these questions is of interest both from a technical and theoretical point of view.

It was also of interest to attempt a clearer explanation of the mode of action of rosin soap in metal-exchange processes. The results of previous work[1,2] indicate that morphological changes occurring on rosination are probably due to the incorporation of the pigment in the micellar structure of the rosin soap and also a consequence of molecular adsorption of rosin on the pigment particles.

As in previous work,[2] CI Pigment Red 49 known as Lithol Red R (I) was taken as a typical pigment in this study.



(I) CI Pigment Red 49, CI 15630 (sodium salt)

2. EXPERIMENTAL

Samples of the sodium salt of CI Pigment Red 49 were prepared as previously. In order to obtain samples of differing physical properties sample 1, after drying, was ground in a typical coffee-grinder. During the preparation of sample 2 the diazotized Tobias acid was washed with distilled water before coupling in order to remove an excess of inorganic salts. Sample 3 was ground sample 2, and sample 4 was derived by recrystallizing sample 1 from 50% DMF. The purity of the prepared samples was estimated by elemental analysis comparing the calculated amount of nitrogen with that found experimentally. Each sample was subjected to X-ray powder diffraction studies (DRON 1,5 apparatus with CuK_αNi-filtered radiation of wavelength 0·154 178 nm). Solubility was found by a gravimetric method and the total surface area by a gaseous chromatographic method.

The studies on the reaction of metal-exchange process were carried out with a dye concentration of $4{\cdot}76 \times 10^{-2}$M (i.e. 20 g dm^{-3}) and a $BaCl_2$ concentration of $2{\cdot}7\times10^{-2}$M. This is in accordance with technical conditions and is equivalent to 1·5 times the theoretical amount. Reaction was also carried out at slightly lower concentrations at lower temperature (11°C) and at a lower pH value (7·05) than in practice.[3] The purpose of this was to slow-down the process and to minimize the errors during the measurements. Before reaction, each sample was dispersed in water for 1·5 h using a mechanical stirrer of constant rpm value. Conversion was calculated on the basis of Ba^{2+} ion concentration, estimated in the reaction mixture by the colorimetric method described by Budesinsky and Vrzalova.[4] Despite some difficulties in applying this method—filtration of reaction-mixture samples was necessary—quite good reproducibility of the results to within ±2% was obtained.

3. RESULTS AND DISCUSSION

For more detailed studies four samples of the sodium salt of the dye (I) were chosen. Their properties are listed in Table 1.

For these samples the degree of conversion, i.e., the exchange of Na^+ for Ba,$^{2+}$ where unity represents complete conversion, is plotted against time in Fig. 1.

All samples after an initial rapid conversion growth during the first 5–10 min. show a definite slow-down of the exchange process. It might be anticipated that one or all of the following processes take place

1. Reaction in solution followed by nucleation and growth;
2. Interchange of cations on solid surfaces;
3. Cation diffusion into sodium salt crystals.

The differences in surface area and solubility of samples 1–3 were very small,

TABLE 1

PROPERTIES OF SAMPLES OF SODIUM SALTS OF LITHOL RED R (I)

Sample	*Total surface area* ($m^2\,g^{-1}$)	*Solubility* ($g\,dm^{-3}$)	*Purity* (%)	*Degree of conversion*			*Intensity of diffraction peaks at 2θ angle values*
				5 min	40 min	120 min	
1	8·1	0·147	96·2	0·75	0·795	0·84	5·2 vs 10·5 s 12·0 m 21–21·8 m 25·5 m 26·5 m 29·5 w
2	8·0	0·143	98·9	0·24	0·285	0·40	
3[a]	8·54	0·143	98·9	0·555	0·656	0·738	
4[b]	0·56	0·102	95·5	0·42	0·465	0·485	5·2 vs 10·5 vs 12·2 m 15·8 s 23 w 25·5 m 28 w 32 w 33·1 w

[a] Sample 3 is ground Sample 2.

[b] Sample 4 is recrystallized Sample 1.

Intensity of diffraction peaks: vs—very strong, s—strong, m—middle, w—weak.

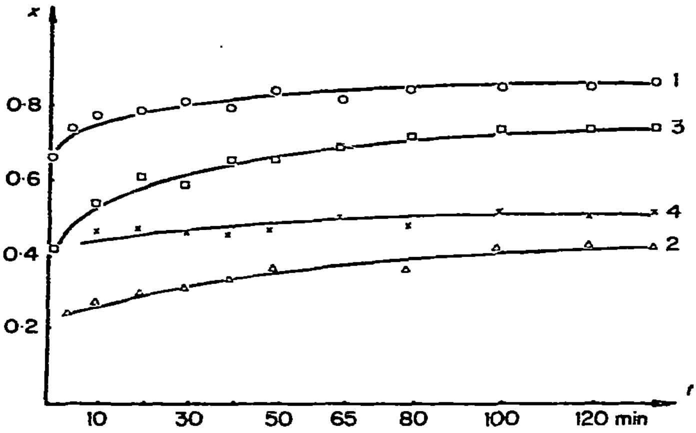


Fig. 1. Degree of conversion of sodium salt of the dye (samples 1–4) plotted against the time of reaction.

however there were definite differences in the degree of conversion of these samples. In the case of sample 4 it should be mentioned that one of the factors which can influence reaction ability is the crystal structure. X-ray diffraction data showed there is an intense peak at 15·8° and weak peaks at 32° and 33·1° which were not present in samples 1–3.

Further work examined the possibility of solid state reactions by a cation exchange mechanism in the crystal. The conversion values obtained for samples 1–4 were checked against some model equations derived for solid state reactions. For this purpose the Jander,[5] Ginstling–Brounstein[6] and Kröger–Ziegler[7] equations were chosen. All have been derived for processes similar to that studied here.

The Jander equation[5] is based on the assumption that the concentration of one of the reactants and the diffusion coefficient are constant. The relation between the reaction rate k_J and the conversion x is given by the following expression:

$$k_J t = \frac{2kDt}{r_0^2} = [1 - \sqrt[3]{(1-x)}]^2$$

where x is the product of reaction after time t, r_0 the particle radius and D the diffusion coefficient.

The Ginstling–Brounstein equation[6] was derived for the same conditions with the assumption that the decrease in the area of the reaction surface is accompanied by an increase in the over-lying layer of the reacted substance, so that:

$$k_{G-B} t = \frac{2kDt}{r_0^2} = 1 - \tfrac{2}{3}x - (1-x)^{2/3}$$

The Kröger–Ziegler equation[7] was derived on the basis of a modification of Jander's assumption. The diffusion coefficient and the rate of growth of the product layer are assumed to be inversely proportional to time as the result of crystal lattice change, so that:

$$k_{K\text{-}Z} \ln t = \frac{2k_J \ln t}{r_0^2} = [1-\sqrt[3]{(1-x)}]^2$$

The results obtained for all these equations are shown in Figs 2, 3 and 4. For the equations given by Jander (Fig. 2) and Ginstling–Brounstein (Fig. 3) only samples 2 and 4 with a low degree of conversion show good agreement between experiment and theory. For samples 1 and 3 with higher conversions values, large differences between Jander and Ginstling–Brounstein equation values and experimental data are observed for longer times of reaction.

In the case of the Kröger–Ziegler equation where the diffusion coefficient is not assumed constant quite good agreement between experimental and theoretical data has been found (Fig. 4). These results suggest that after the first 5–10 min. of the reaction, it continues by a process of ion replacement in crystal lattice, in other words solid state reaction.

The diffusional character of this process was confirmed by experiments in which a doubled concentration of barium chloride $5{\cdot}4\times10^{-2}$M (i.e. $2{\cdot}3\times$theory) was used (Fig. 5). The observed increase in the conversion rate is

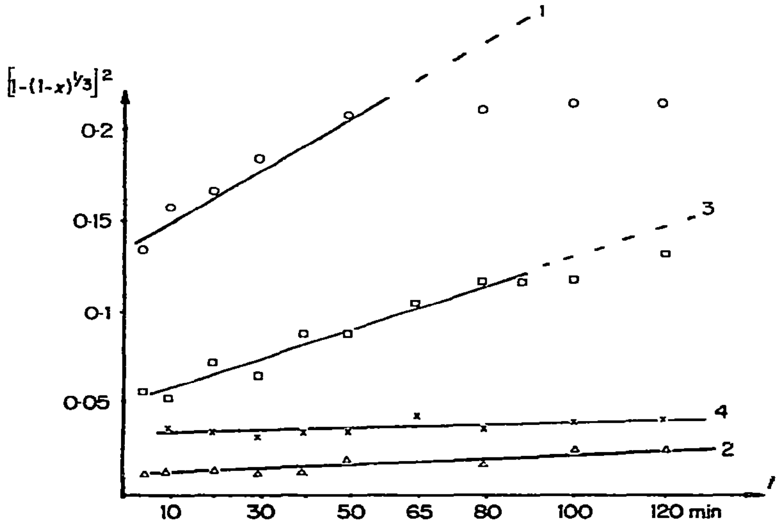


Fig. 2. Approximation of experimental data to Jander equation.

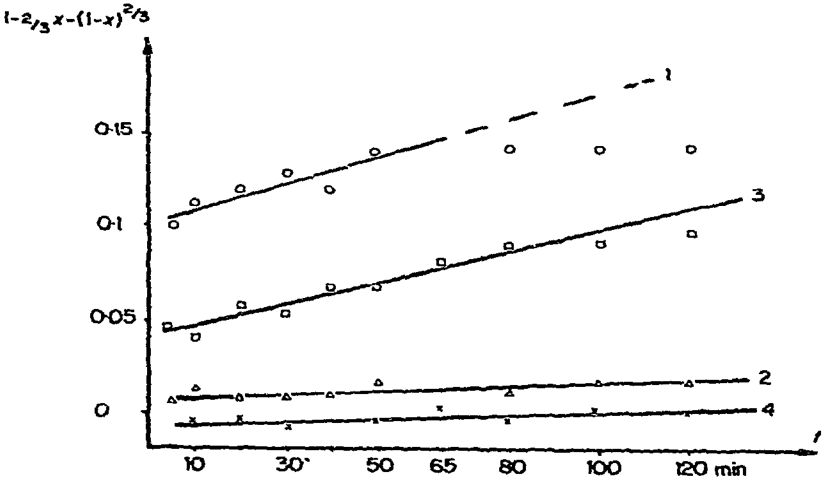


Fig. 3. Approximation of experimental data to Ginstling–Brounstein equation.

in good agreement with Fick's first law for diffusion processes:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = D\frac{\Delta c}{\Delta y}$$

The possibility that 20–30% of the reaction can proceed through a solid state diffusion reaction may then well explain the importance of the physical properties of the sodium salt.

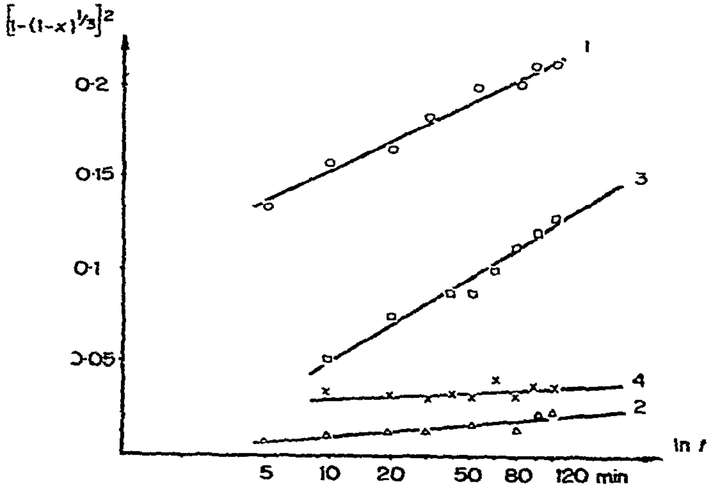


Fig. 4. Approximation of experimental data to Kröger–Ziegler equation.

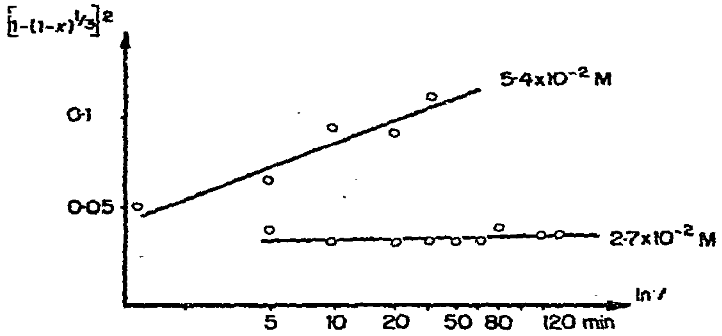


Fig. 5. Effect of concentration of barium chloride on conversion rate of sample 4 (Kröger–Ziegler equation).

The same method has also been applied to the study of the influence of rosin soap on the metal-exchange process.

In Fig. 6 there are shown the conversion values obtained for samples 1–4 when rosin was present (concentration of rosin $6{\cdot}3\times10^{-3}$M i.e. 10% by weight of sodium salt or 0·13 moles of rosin per mole of the dye). In all cases an increase in the degree of conversion can be observed when compared with data in Fig. 1. For sample 2 which shows the lowest conversion value in the absence of rosin the influence of the concentration of rosin below (2×10^{-5}M) and above (4×10^{-4}M) its critical micelle concentration (CMC) values[2] has been also examined. Conversion values and Kröger–Ziegler equation values are shown in Figs 7 and 8.

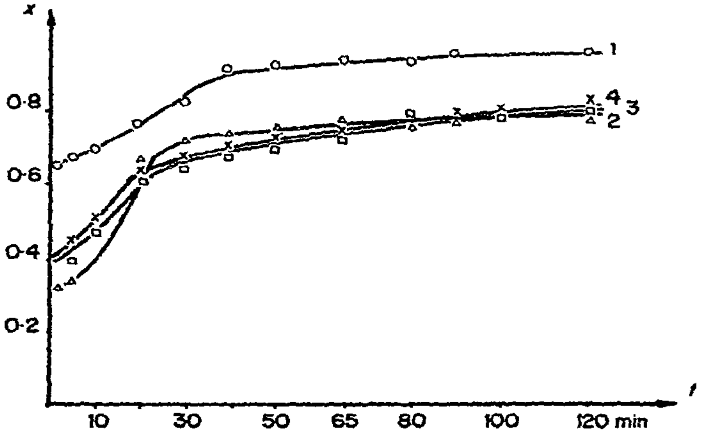


Fig. 6. Effect of rosin on conversion of samples 1–4.

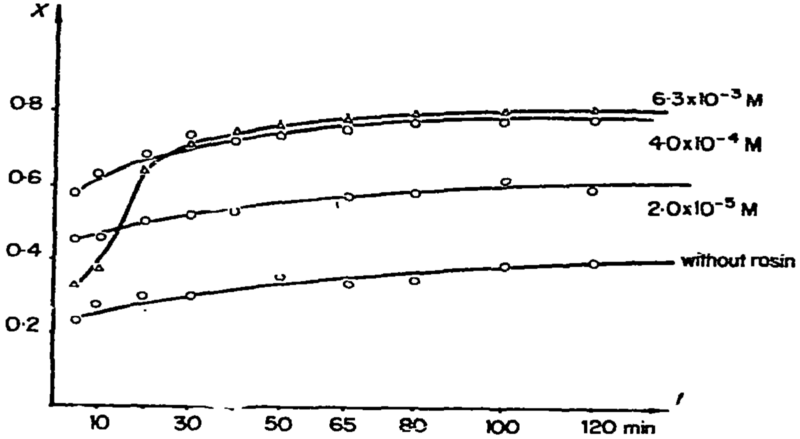


Fig. 7. Effect of varying concentrations of rosin on the degree of conversion of sample 2.

The results are very interesting. It can be observed that addition of rosin soap yields both an increased conversion (Fig. 7) and an increase in the conversion rate estimated on the basis of the Kröger–Ziegler equation (Fig. 8). It may thus be anticipated that the specific influence of rosin is probably due to the increased solubility of the dye by micellization. This phenomenon, by increasing the conversion rate, leads to the formation of plate-like friable particles with higher tinctorial strength. It has to be mentioned however that the influence of rosin is also apparent below its CMC value, as was also

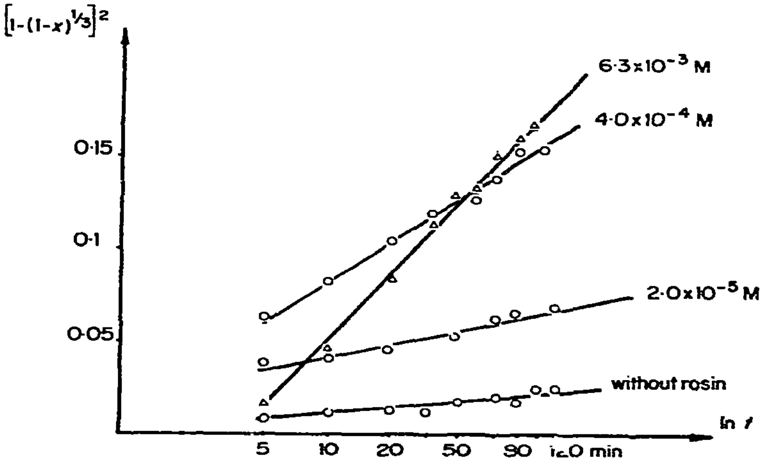


Fig. 8. Effect of concentration of rosin on conversion rate of sample 2 (Kröger–Ziegler equation).

previously observed by X-ray diffraction and Scanning Electron Microscopy methods. The latter phenomenon and the effect of some slow-down in the rate of the reaction at the highest concentration of rosin during the first 10–20 min. (Fig. 6) are still difficult to explain.

The result of the above work, although not directly relevant to commercial practice, does allow a closer understanding of the complicated metal-exchange process during the preparation of toners. The assumption that at some stage this process can run through solid state diffusion reactions could also allow the formulation of conclusions of practical importance.

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