204. *Selective Diffusion into Ion-exchange Resins. A New Method for the Purification of the Direct Cotton Dyes.*

By R. W. RICHARDSON.

Purification of direct cotton dyes by an ion-exchange technique is described. Use is made of the observation that selective diffusion of ionic species into the bulk of the resin structure depends on the molecular dimensions of the ion. It has been shown that by this means the large organic anions of the dye may be effectively separated from those of the much smaller diluent salts.

ISOLATION of pure direct cotton dyes from the crude salted-out products is an essential preliminary to all experiments on the fundamental physical chemistry of dyeing. For this purification Robinson and Mills (*Proc. Roy. Soc.*, 1931, *A*, **131**, 596) recommended a procedure which has since been adopted by *inter al.*, Boulton, Delph, Fothergill, and Morton (papers, from 1935 onwards, in *J. Text. Inst.*, *J. Soc. Dyers Col.*) in their quantitative investigations. This method consists in repeated precipitation of the dye from aqueous solution by pure sodium acetate until free from inorganic anions, followed by extraction of the dried dye with ethanol to remove the acetate. The method is tedious, often involving filtrations of near-colloidal precipitates; further it has now been shown that prolonged extractions are needed to remove last traces of sodium acetate; varying amounts of the dye itself are often removed during this treatment depending on the nature of dye, its moisture content, and the purity of the ethanol.

The purifications described below are based upon the fact that the ion-exchangers used are capable of acting as " molecular sieves." The resins contain a network of pores of various sizes, as is shown by an increased capacity as the size of the adsorbed molecule is reduced. It has been shown (Richardson, *Nature*, 1949, **164**, 916; Faraday Soc. Discussion, Chromatographic Analysis, 1949, p. 159) that ions of an average diameter of about 30 A., corresponding approximately to those of the direct colours based on benzidine derivatives are, in effect, completely prevented from entering the resin. Reaction takes place at the surface but this corresponds to $<0{\cdot}1\%$ of the available exchange centres. While molecular-sieve effects determine in varying degrees the behaviour of all molecules in contact with porous solids, only in the case of gases have separations by a total (*i.e.*, a completely selective) sieve action been recorded (Barrer, *Quart. Reviews*, 1949, **3**, 293). Ion-exchange resins of well-defined micropore size should thus have extended usefulness by virtue of a new, and variable, physical property.

FIG. 1.

Absorption of Sky Blue FF on Deacidite B; 2 g./25 ml.; 25°.

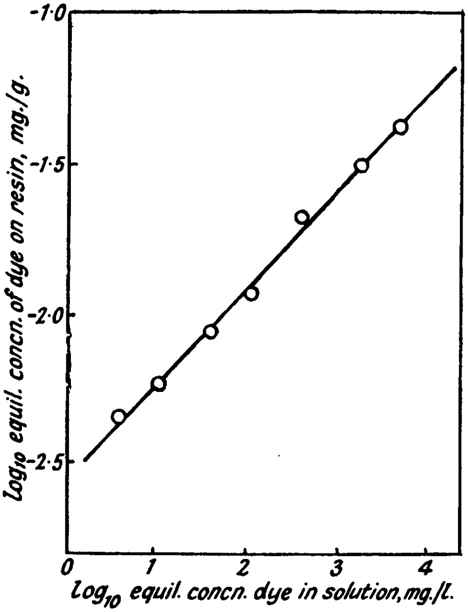
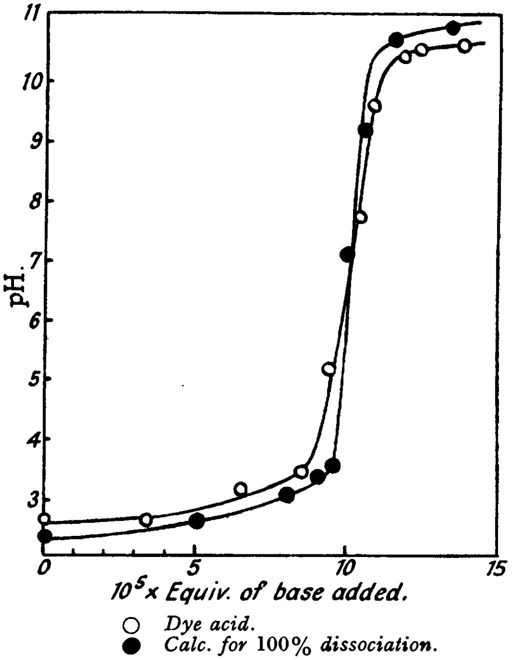


FIG. 2.

Titration curve for Sky Blue FF acid (10^{-4} *equiv. in* 20 *ml.*).



Exchange from aqueous solutions of the crude dyes on a sulphonic acid resin gave acidic, ash-free effluents containing the derived dye acid and the inorganic acids from the salts. The solutions, with either a weakly or a strongly basic exchanger, yielded effluents from which the inorganic acid alone had been removed.

The use of a strongly-basic resin to remove carbon dioxide was later found necessary. Even in the absence of carbonate impurity, dissolved carbon dioxide on neutralisation may yield sufficient alkali carbonate to represent several % of impurity calculated on the weight of pure dye.

Many dye coupling components containing ionisable groups are sufficiently small to be essentially completely adsorbed in the quantities in which they would normally be expected to be found. For example, 2-aminonaphthalene-1-sulphonic acid is able to reach **94%** of the ionic centres available to sulphuric acid in the weakly basic resin Deacidite B (Richardson, *loc. cit.*). With dyes smaller than those based on benzidine, *e.g.*, those of the " acid " class prepared from the naphthylamines, as much as 1·5% of the resin capacity may be saturated. Regeneration of the resin then becomes troublesome as the slow outward diffusion of the dye makes its complete removal difficult. With the materials available, however, it was possible to purify sodium 8-acetamido-1-hydroxy-2-phenylazonaphthalene-5-sulphonate by increasing the rate of flow of solution through the column.

FIG. 3.
Titration curve for the carboxylic dye Chlorazol Fast Red F (250 *mg.*/100 *ml.*).

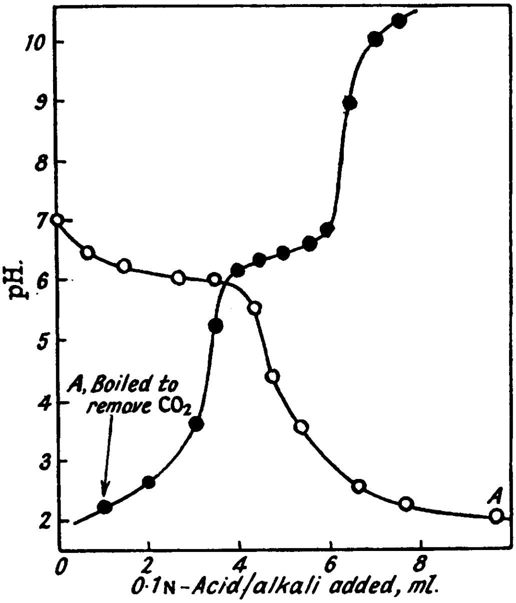
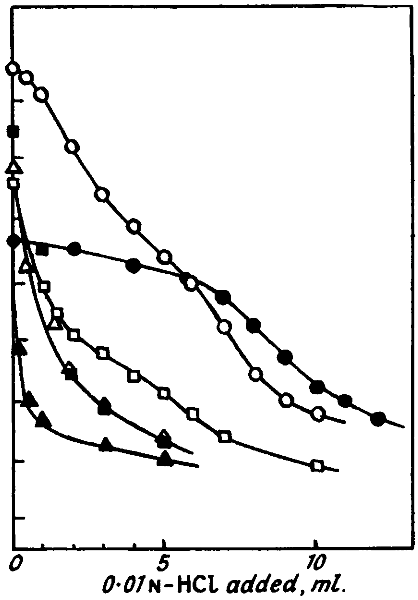


FIG. 4.
Electrometric titration of Sky Blue FF preparations.



For 100 *mg. of dry dye.*
○ *Crude dye* (250 *mg.*).
● *Cf.* (5), *Table.*
■ *Cf.* (3) ,,
□ *Cf.* (4*a*) ,, (*ash*, 29·5%).
△ *Cf.* (2) ,,
▲ *Calc. for* 100% *dissociation*

The small surface adsorption noted for the larger ions was shown to be that characteristic of the Freundlich type (Fig. 1) and is therefore similar to the behaviour of the much smaller inorganic acids in aqueous solution (Myers, Eastes, and Urquart, *Ind. Eng. Chem.*, 1941, **33**, 1270).

The sodium salts of the dye acids were prepared by neutralisation with alkali hydroxide to pre-determined pH values. These were found to be pH 7 for sulphonic acids and pH 8 for those dyes also containing carboxyl groups (Figs. 2 and 3). The removal of alkali, added in excess, by weakly acidic resins containing phenolic hydroxyl or partly saturated carboxyl groups was unsuccessful. Both types of exchanger exhibited a small " salt-splitting " capacity, giving solutions of sufficient acidity (pH 3—4) to affect the dye-absorption characteristics of some classes of dyes. The effluents obtained were, however, more easily adjusted to the correct pH values than the original strongly acid solutions.

With dyes yielding water-insoluble sulphonic acids exchange from aqueous-organic solvents was unsatisfactory, owing to the necessity for the removal of the organic solvent when recovery of the solid dye was otherwise not required. For these and for " acid-labile " dyes the alternative " reverse deionisation " using strongly basic exchangers was therefore examined, since the solutions under these conditions remain alkaline. It was concluded that if the molecular-sieve effect was shown with this type of resin (their use in the acid-absorption experiments in place of the weaker resins, described above, had not then been investigated) an effluent containing the dye (sodium salt) and alkali hydroxide should result.

This was found to be the case: only slight, apparently irreversible or very slowly reversible, adsorption takes place with large dye molecules. Less than 0·5% of inorganic salts, based on the weight of dye, was detected in the effluent. The removal of excess of alkali was then carried out as previously described. During this work it was found necessary to prevent carbonation of the alkaline effluent since buffering caused by alkali hydrogen carbonate made final pH adjustment impossible. Alkali carbonate if present in the crude dye is removed by the strongly basic resin (Davies and Nancollas, *Nature*, 1950, **165**, 237).

The ash contents recorded for the typical dyes examined (Sky Blue FF, Colour Index No. 518) were less than those obtained in routine preparations by the sodium acetate method. It was then shown (Fig. 4) that in the latter preparations small amounts of sodium acetate were retained even after 7 hours' rapid Soxhlet extraction. The lowest ash content obtained by this method was 0·5—1·0% higher than that obtained by ion exchange. The sample then still contained traces of sodium acetate which was shown to be difficult to remove unless the dye was kept finely divided during extraction. The analytical values suggest that the overall degree of sulphonation of the dye sample was less than theoretical; the naphthol-sulphonic acid component would be expected to contain less rather than more than the theoretical amount of SO_3H since the lower-substituted naphthalenes will be those preferentially isolated on salting-out during recovery; the low result was shown not to be inherent in the method of analysis.

The methods outlined may not be generally applicable. For example, non-ionic impurities may be present (these can be removed by solvent extraction before exchange) and there may be functional groups within the dye which are labile in contact with the exchanger. Modifications in the technique of selective adsorption should be possible, however, for most dyes. The technique of "mixed-bed" deionisation can give the corresponding dye acids provided that they are soluble under acid conditions.

Added in Proof.—Since this paper was prepared Deuel, Solms, and Anyas-Weisz (*Helv. Chim. Acta*, 1950, **33**, 2171) have given examples of the quantitative separation of large polymeric anions [*e.g.* poly(galactur-onic acid)] from the related monomers by methods similar to those described above.

EXPERIMENTAL.

The capacity of each column was determined for 0·05N-solutions—sodium chloride for the strongly acid (effluent aliquots being titrated) and strongly basic resins (the effluent being examined for chloride ions), and sodium hydroxide for the weakly acid exchangers (pH measurements showing the break-through). The capacity was also determined by carrying out a trial run with the appropriate crude dye. Ash contents were determined on effluent aliquots; or the dye was precipitated and the filtered solution examined for residual anion. The effectiveness of the base-absorbing resins was determined by pH measurements and, with some dyes on lightly coloured resins, visually, a colour change being observed at the dye/dye–alkali junction.

All ashes were sulphated; the values recorded are calculated for samples dried at 140°/15 mm.

Before analysis the solutions were filtered to remove any insoluble impurity derived from the column material.

The following details for Sky Blue FF (Colour Index No. 518) are typical of those employed for a sulphonic acid direct cotton dye. The concentrations given are probably maximal for efficient exchange; the optimum rate of flow of solution was not examined. (i) An aqueous solution (850 ml.) of the dye (*ca.* 55% pure; diluent sodium chloride, 10 g./l. = 0·084 total equiv.) was passed through a column of sulphonic acid resin (A) (length, 50 cm.; diameter, 1·95 cm.; capacity for dye acid with ash $\not>$1%, 0·088 equiv.) in the acid form during 4 hours. The acid effluent (inorganic acid = 0·065 equiv.) was then passed through a column of strongly basic resin (D) (length, 50 cm.; diameter 1·35 cm.; capacity, 0·075 equiv.) in the basic form during 6 hours. The dye acid, isolated on evaporation, was obtained as a bright, brassy mass, m. p. *ca.* 210° (decomp.) (Found: ash, 0·5%). Excess of N-sodium hydroxide (20 ml.) was then added, and the solution passed through a column of weakly acid resin (C) (length, 55 cm.; diameter, 1·95 cm.; the resin was regenerated in the usual way, washed, and taken to the break-through with 0·05N-sodium hydroxide, again regenerated to the break-through with 0·05N-hydrochloric acid, and finally washed with water to remove chloride and to give an effluent pH 4·5; subsequent regenerations were made with the dilute acid only). The pure dye was isolated from the effluent (pH 5·0, adjusted by 0·1N-sodium hydroxide to pH 7·0) as bright coppery lumps (Found: ash, 26·9%).

(i *a*) A similar alkaline solution of the dye acid, passed through a column of carboxylic acid resin (B), length, 25 cm.; diameter, 1·35 cm., regenerated, treated with 350 ml. of N-sodium chloride, and washed free from chloride at each regeneration, gave an effluent (pH 4·0) which yielded the dye (Found: ash, 25·5%).

(ii) The dye solution (2·5 l.; 5 g./l.) was passed through a column of strongly basic resin D [length, 100 cm.; diameter, 3·3 cm.; total capacity of column *ca.* 5·5 l. (5 g. of dye per litre)] in the basic form, and the resin (C), in series, during 5 hours. The dye was isolated from the effluent (pH 5·2, adjusted to 7·0) as before (Found: ash, 27·2%).

(iii) With acid-insoluble dyes containing much carbonate impurity the solutions were first treated with the strongly basic resin (D) and then adjusted to a pH 4 by treatment with the carboxylic acid resin (B). The liberated carbon dioxide was then removed by re-passage through resin (D).

The results of purifications of this dye are summarised in the table.

Method.	pH of final soln.	Ash, %.	Comments.
(1) Sulphonic acid resin (A); strongly basic resin (D); + NaOH (excess); weakly acid (phenolic hydroxyl groups) resin (C)	4·75	25·5	
	adj. to 7·0	26·9	—
(2) Resin (D); resin (C)	5·0	26·0	10% of $NaHCO_3$ added as diluent to crude dye in one run
	adj. to 7·0	27·2	
(3) Resin (D); carboxylic resin (B); resin (D); + NaOH (excess); resin (C)	4·2	—	+ 10% of $NaHCO_3$
	adj. to 7·0	26·0	
(4) (*a*) Prepared by method of Robinson and Mills	—	31·1	~3·5% NaOAc, calc. as Na_2SO_4
(*b*) Sample from (*a*) reground and re-extracted	—	27·7	<0·5% NaOAc
(5) Resin (D); resin (C). No exclusion of carbon dioxide	—	32·1	~6% $NaHCO_3$, calc. as Na_2SO_4
Calc. for the pure dye	—	28·6	—

Resin (A), Zeokarb 215 (Permutit Co.)
Resin (B), Zeokarb 216 ,,
Resin (C), Zeokarb 237/30 ,,
Resin (D), Deacidite F (Permutit Co.)
Resin (E), Deacidite B ,,

At 2·5 g. of pure dye per litre pH 5 represents 4—5% of unneutralised dye acid, and pH 6 represents 2% (values calc. from Fig. 2).

(iv) Pure Benzopurpurin 4B (Colour Index No. 448) was similarly obtained by method (ii) (Found : ash, 17·9. Calc. for the pure dye : ash, 19·6%). Prepared according to Robinson and Mills, the dye contained 18·8% of ash and was shown by electrometric titration to contain ~1% of sodium acetate even after repeated ethanol extractions. After further purification through resin (D) and resin (B), the ash content was 18·4%.

(v) Pure Chlorazol Fast Red (Colour Index No. 419), a carboxylic acid-substituted dye, was also obtained by method (ii) (Found : ash, 22·9. Calc. for the pure dye, ash, 22·7%). Prepared according to Robinson and Mills, the dye had 24·0% of ash.

(vi) Sodium 8-acetamido-1-hydroxy-2-phenylazonaphthalene-5-sulphonate. The crude reaction product (from 15 g. of naphthol) was precipitated with acid, filtered off, and dissolved in water (2 l.). The solution was then passed through the acid resin (A) column, as in (i), during 4 hours and through the large resin (D) column, as in (ii), during 15 minutes. The final effluent was then adjusted to pH 7·0 (Found : ash 16·7. Calc. for the pure dye : ash, 17·4%).

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