Thermofixation of Dyes on Synthetic-polymer Fibres and their Blends

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Presented at a Symposium held by the Manchester Section in the Lesser Free Trade Hall, Manchester, on 8th March 1963, Mr. A. S. Fern in the chair

After an introduction outlining the advantages of continuous processing, practical details are given of the vital stage of cloth preparation. Suitable methods and machinery for the process are then considered. The fixation of various classes of dye on synthetic-polymer and cellulosic fibres, and on their blends, is discussed. Particular attention is given to the behaviour of dyes under thermofixation conditions and the effect of heat on certain synthetic-polymer fibres is indicated. The dyeing of narrow-width fabrics by the thermofixation technique is discussed, with reference to suitable equipment. The final section deals with the fixation of pigments on textile fibres and blends by resin-bonding. The absence of fibre substantivity in this method enables solid dyeings to be produced readily on fibre blends.

Introduction

The introduction of synthetic-polymer fibres to the textile industry posed a number of processing problems. Existing dyeing procedures had to be considerably modified, and one result of the search for more satisfactory dyeing methods was the thermofixation technique, first developed by du Pont under the trade-name Thermosol [1–3]. The process consists in the application of dye by padding, development at a high temperature, and scouring to remove excess or unfixed dye. Although originally devised for use with synthetic-polymer fibres, this process has since found wider application, being used, for example, in the fixation of reactive dyes on cellulosic fibres.

In general, synthetic-polymer fibres have highly crystalline molecular structures which are less readily penetrated by dye molecules than those of cellulosic and protein fibres. Disperse dyes [4] are widely used for dyeing them and are applied as fine aqueous dispersions. The rate of diffusion of these dyes into the fibres can be increased by raising the temperature, since at higher temperatures the mobility of dye molecules is greater and the movement of polymer chains in the amorphous regions of the fibre increases [5]. For example, a dyeing that may require several hours to produce at 100°C can be obtained in less than 1 h at 130°C and in 20–60 s at about 200°C.

The use of very short dyeing times at temperatures near 200°C forms the basis of the Thermosol process [6]. Amongst the advantages claimed [7–9] for this process are that—

(*a*) it is continuous and thus large yardages can be dyed economically,

(*b*) in many cases, the use of carriers and swelling agents can be avoided, reducing the danger of spotting and the adverse effect of some carriers on light fastness,

(*c*) colour yield is excellent, e.g. 75–90% for disperse dyes on polyester fibres,

(*d*) fabric is processed in open width, eliminating rope marks,

(*e*) heat setting and dyeing may be carried out simultaneously, and

(*f*) many levelling difficulties can be avoided, because application by padding gives even coverage of all fibres and the dye diffuses rapidly into the fibres at the high fixation temperatures employed.

The following scheme is an indication of that envisaged for dealing with a blend such as Terylene (ICI)–cotton

> Desize–scour–dry–brush–crop–singe–bleach–mercerise–dry–pad–dry–thermofix–scour–dry–finish.

The general principles cover other blends, however, with modifications depending on the fibres present.

Cloth Preparation

Open-width preparation is always desirable for cloth that is to be dyed by the pad–thermofix process, although rope preparation is permissible if the cloth is heat-set in open width before being padded. Size and other extraneous matter should be removed before any heat treatments, e.g. singeing, are given, since these can fix the impurities in the fibre. With synthetic-polymer fibres, singeing before dyeing may cause beads of polymer to form on the fabric surface. These beads may subsequently dye more heavily than the rest of the fabric [8, 9].

Fig. 1 is a photomicrograph of such a bead of Terylene, exhibiting preferential adsorption of dye. This occurred during dyeing at the boil for 90 min in the presence of *o*-phenylphenol as carrier. The fabric, in this case a Terylene–cotton blend, had been badly singed during preparation, and the result of carrier dyeing is shown on the left of Fig. 2. The adjacent piece of fabric was taken from the same badly singed piece and dyed with the same dyes, but using a thermofixation process. The result was perfectly level (see Fig. 2). Thus, when dye is padded and dried evenly on the fabric, and diffusion is so accelerated that complete penetration occurs within seconds, there appears to be no opportunity for preferential adsorption of dye into the polymer beads. Bead formation on singeing is diminished if the amount of surface fibre is reduced to a minimum during brushing and cropping. As singeing tends to give the fabric a rather harsh handle, it should be followed by a wet process.

Bleaching is generally necessary only for blends containing cellulosic fibres. Occasionally nylon 6.6 has to be bleached if it has become yellow during

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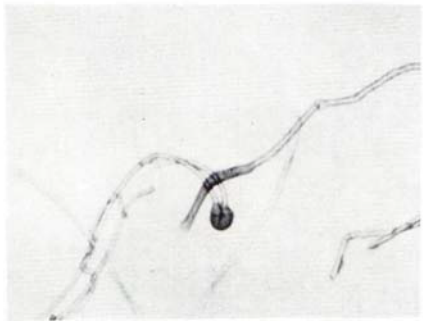
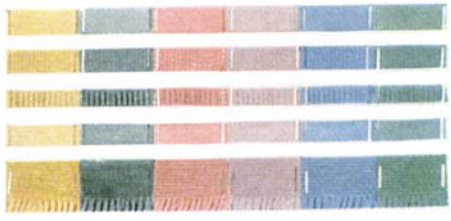


FIG. 1— Photomicrograph of heavily dyed Terylene bead, caused by singeing before carrier dyeing

carrier-dyed pad–thermofix

FIG. 2— Effect of faulty singeing before carrier and pad–thermofix dyeing on Terylene–cotton fabric



a Tricel *b* Dicel–cotton (50 : 50)
c nylon–viscose rayon stretch (50 : 50)
d nylon–viscose rayon (50 : 50)
e Tricel–cotton (50 : 50)

FIG. 9— Microfix dyeings on different fibre blends (identical pad-liquors; 5 min at 150°C)

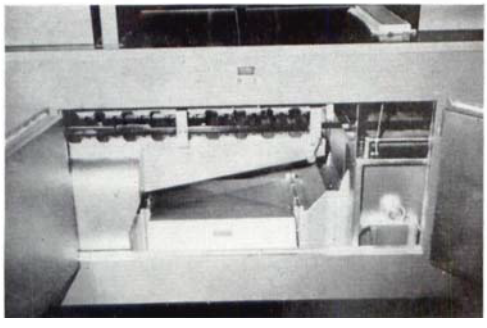


FIG. 3— Benz laboratory-scale drying and thermofixation unit, showing fabric passing through on pin-frame

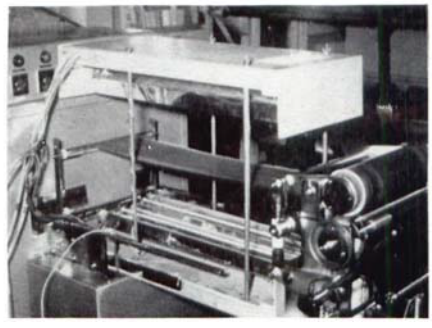


FIG. 4— Padding, infrared preliminary drying, and completion of drying on Benz laboratory-scale equipment

setting. Usually only fabrics made from blends containing cellulosic fibres are mercerised before being dyed. This treatment improves the coverage of immature cotton and increases the dye uptake, which is desirable if heavy depths are required. Caustic soda concentrations of 42°Tw.[10] and 53°Tw.[15] have been suggested for use in mercerisation of Terylene–cotton blends. Neutralisation should follow mercerising, with drying being carried out to fixed width, although the use of cans is sometimes permissible.

These preparatory treatments should produce a crease-free fabric which wets out evenly and instantly on entering the pad-liquor. Blend fabrics containing hydrophobic fibres have a fairly low water imbibition and hence the associated fibre, usually cellulosic, must have high absorbency. Surfactants are used to bring about quick, even penetration into the interstices of synthetic-polymer-fibre fabrics.

Dyeing

The dyeing stage consists of pad–dry–thermofix. The machinery for this stage can be tailored to the requirements of each processor. Certain general principles are, however, apparent. For padding, both two- and three-bowl mangles have been used successfully. The degree of hardness of the rubber bowls depends on both the fibre used and the fabric construction. Very thick materials, e.g. webbing for car safety harness, require the use of soft bowls in order to avoid carry-through of liquor at the edges. Two-sided effects on the material may be produced if bowls of differing hardness are used.

Drying is best carried out in two stages—

(*a*) an infrared unit for preliminary drying, followed by

(*b*) completion of drying, utilising either hot air or contact with hot metal, e.g. steam-heated cylinders.

Infrared heating is the best method of removing water without causing migration of dye. Only 30–40% of the total moisture need be removed to eliminate virtually all migration. Hot air or metal-contact dryers all operate by evaporating water from the fibre or fabric surface. The surface water is then removed as vapour, and more water is drawn to the surface to restore the equilibrium between liquid and vapour. Migration of dye particles to the surface may occur as a result of this movement of water. Any difference between the rates of drying of the two faces of a fabric would therefore give a two-sided appearance. Infrared radiation, however, is absorbed not only by the water but also by the fibres themselves, and the water is evaporated within the fibres and fabric. Thus the movement to the surface is of water vapour, not liquid, and therefore the dye cannot migrate to the same extent.

The use of infrared heating to obtain a residual moisture content of about 70% of the original enables other types of drying equipment to be used to complete the removal of moisture, with little danger of migration or marking-off occurring. Flue dryers are very satisfactory for this stage and, more recently, Teflon-coated cans, arranged in ascending order of temperature, have been reported to give good results[10]. One drawback to the use of cans, however, is the lack of the width control which is usually essential in a commission dyehouse, unless setting has been carried out before padding.

Thermofixation is best carried out by means of a flue baker, which gives a far higher rate of production than a stenter. It is essential that heat transfer should occur at the same rate on both faces of the fabric and that the temperature be uniform across the piece. This latter condition is sometimes difficult to satisfy in stenters, especially at temperatures near 200°C, and the temperature at the selvedges may be considerably lower, although the most modern equipment generally overcomes this defect. Under these circumstances, there is a good case for passing the material quickly through an infrared zone, immediately after the exit from the stenter, to give even dye fixation from edge to edge. Although flue bakers do not, in general, suffer from the same drawback, they lack width control and allowance would have to be made for this. Superheated cans have been used satisfactorily[11, 15] where allowance has been made for cloth shrinkage.

After thermofixation, open-soaping or scouring on a winch effectively removes unfixed dye. For certain heavy dyeings, a reduction clear may be necessary. If maximum fastness is to be achieved, it is essential to wash the material thoroughly to remove all surplus dye, thickener, and assistants.

Laboratory Techniques

The problem of colour matching and the correlation between laboratory and bulk working are often said to be major drawbacks to the continuous thermofixation process. In our investigations, good agreement has been obtained between bulk working and laboratory matchings prepared using a Benz drying and thermofixation unit[12].

In this machine, the conditions simulate very closely those found in full-scale hot-air baking units (see Fig. 3 and 4). Electrically heated air impinges on both faces of the fabric from nozzles shown in Fig. 3. A damper allows the proportion of air passing through either set of nozzles to be varied, so that there is a perfectly balanced flow over both surfaces of the fabric. This laboratory-scale machine can be used under a wide range of conditions, and cloth may be treated for periods of 12·5 s and longer, at temperatures up to 245°C. The duration and temperature of treatment can be accurately controlled and the machine can be used either for various sizes of small patterns on a pin-frame or for continuous lengths. The maximum width of fabric on the machine illustrated is approximately 10 in. (although other units have a maximum width of 18 in.). A very satisfactory laboratory arrangement for thermofixation trials consists of a two-bowl vertical padding mangle, followed immediately by an infrared preliminary drying zone, with final drying and thermofixation carried out on the Benz unit (see Fig. 4). Washing-off is carried out separately, using a batchwise technique.

Types of Dye Used

With the above laboratory apparatus, investigations have been made into the performance of various classes of dye on many types of fibres, viz.—

(1) disperse,
(2) vat,
(3) 1:2 metal-complex and milling acid, and
(4) reactive dyes.

DISPERSE DYES

Disperse dyes are the most widely used class for synthetic-polymer fibres. The severe conditions of the process limit the number of dyes that are satisfactory. The dyes must not be affected by the heat treatments to which they are subjected during thermofixation, i.e., they must not decompose or sublime off the fabric and condense on the machinery. Generally, disperse dyes of high sublimation fastness also give dyeings of good fastness to wet processing. For application by padding, disperse dyes must give very fine aqueous dispersions which are stable for some hours in the presence of a thickening agent. Thus only the very finely dispersed forms should be used. When a blend fabric, e.g. Terylene–cotton, is being dyed with a mixture of disperse and reactive dyes, in a single pad-liquor, soda ash is used to promote fixation of the reactive dye on the cellulosic component, so that the disperse dyes must be stable to this alkali. Certain dyes, e.g. C.I. Disperse Red 55, change colour in presence of alkali.

The behaviour of several disperse dyes on Terylene under thermofixation conditions has been investigated, using the Benz unit. Since the conditions of time and temperature for the application of disperse dyes to polyesters are more severe than those likely to be encountered with other types of fibre, dyes found suitable for polyester fibre should also be suitable for the others.

A length of spun Terylene fabric (previously prepared) was padded through a dispersion containing—

	(g/l.)
disperse dye	*x*
urea	50
Manutex LO (sodium alginate: Alginate Industries)	5

The pick-up was approximately 60%. Drying was carried out on the Benz unit at 100°C. Pieces of fabric were then thermofixed for from 12·5 s to 180 s at 170–230°C. Scouring for 15 min at 95°C in a solution of Ultravon JU (CIBA) (2 ml/l.) completed the process.

Dye fixation was estimated by stripping the dye from a known weight of fabric, using identical amounts of dimethylformamide. Solutions of dye in dimethylformamide were estimated colorimetrically. To avoid errors due to differences in pick-up at the pad, colorimetric standards were obtained by stripping the dye from given weights of the padded and dried but unfixed material. All colorimetric measurements were made on the Unicam SP 700 recording spectrophotometer.

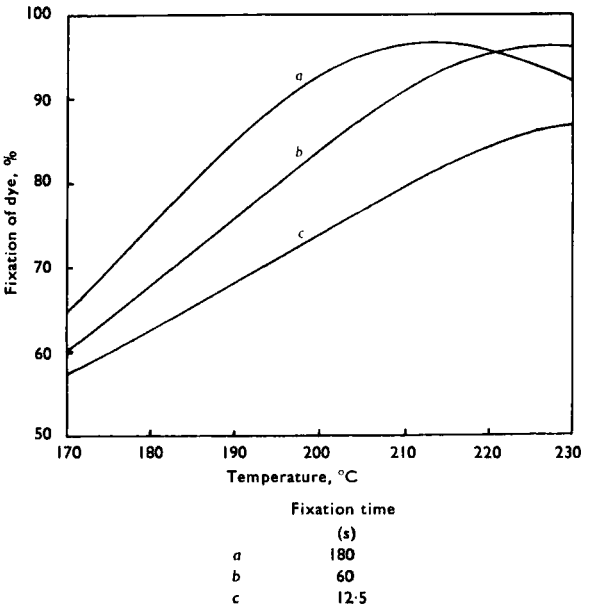


FIG. 5— Fixation of Terasil Brilliant Yellow 3GL on Terylene

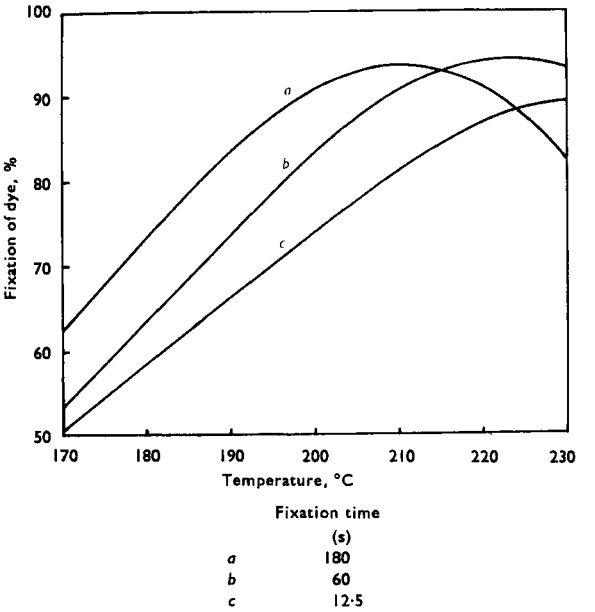


FIG. 6— Fixation of Terasil Brilliant Pink 2GL on Terylene

Graphical interpretation of results (see Fig. 5–8) indicates that the optimum thermofixation conditions for a particular dye are largely dictated by its rate of diffusion, which is related to molecular size. It will be seen from Fig. 5 that a minimum temperature of 200°C is necessary to fix Terasil Brilliant Yellow 3GL (C.I. Disperse Yellow 65) and the optimum time for fixation at 200–210°C is about 60 s. At shorter times, fixation is incomplete unless higher temperatures are used. If the temperature exceeds 210°C for longer times, colour yield decreases. This is due to sublimation of the dye, which under normal conditions has good sublimation fastness. Similar results have been obtained with a fluorescent brightening agent. Uvitex ERN (CIBA), on Terylene[13]. A similar

result is obtained with Terasil Brilliant Pink 2GL (C.I. Disperse Red 86) (Fig. 6) but a slightly different one with Terasil Blue GF (C.I. Disperse Blue 54), which diffuses more rapidly (Fig. 7). Results at short fixation times follow those obtained for Terasil Brilliant Yellow 3GL and Pink 2GL at 170–230°C. For times of the order of 60 s, a higher fixation is obtained and the effect of temperature is generally not so pronounced as with the other dyes. For fixation times of 3 min, the colour yield gradually decreases with increase in temperature, owing to sublimation of the dye.

Experiments to compare the relative fixation of disperse dyes possessing (*a*) slow, (*b*) medium, and (*c*) rapid rates of diffusion have been carried out. The results are shown in Fig. 8. These curves indicate only the degree of fixation for a time of 60 s over the temperature range 170–230°C, but they confirm that the molecular sizes of the dyes are very important. C.I. Disperse Yellow 65 (type *a*) shows increasing fixation over the whole temperature range. C.I. Disperse Red 11 (type *b*) gives a maximum value for fixation and then shows slight signs of sublimation. C.I. Disperse Orange 3 (type *c*) shows pronounced signs of sublimation over the whole temperature range. The high temperatures used did not cause decomposition of these dyes, as shown by a comparison of absorption spectra of solutions of untreated dye and solutions made from dye that had been heated at 240°C for 4 min.

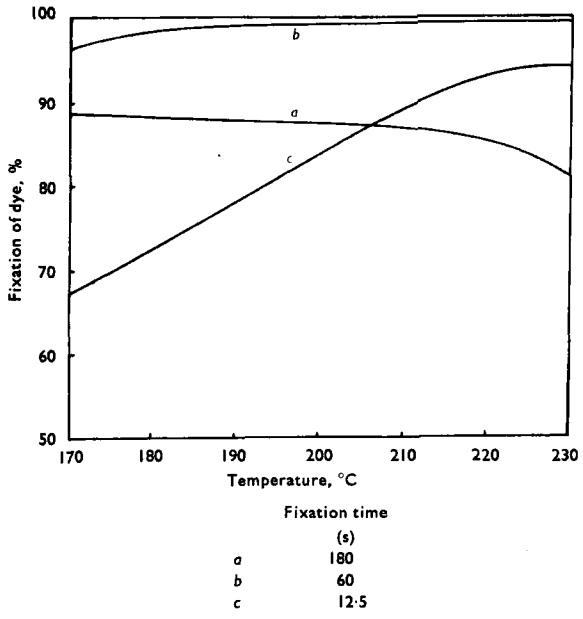


FIG. 7— Fixation of Terasil Blue GF on Terylene

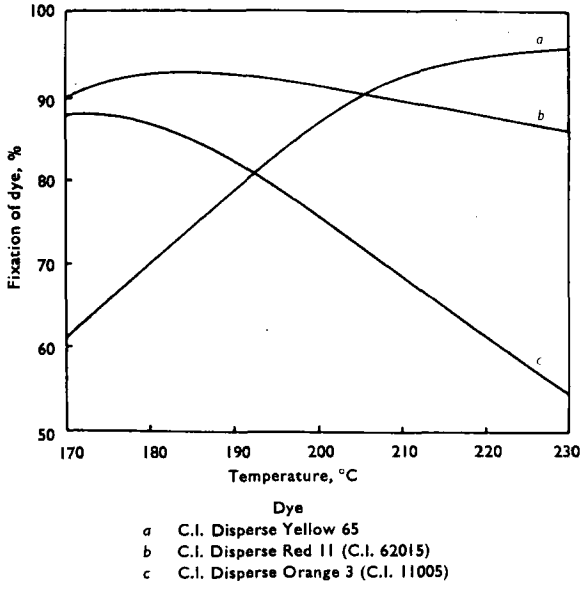


FIG. 8— Fixation on Terylene of disperse dyes of differing diffusion rates in 60 s

VAT DYES

Vat dyes have been used for dyeing synthetic-polymer fibres, notably polyester fibres and polyester–cotton blends, by a thermofixation technique [6, 7, 9, 10, 14, 15], although heavy dyeings are not readily attainable. Certain vat dyes on polyester fibres give dyeings of very high fastness. The physical form of the vat pigments is very important, and it is essential to use the very finely dispersed form to avoid specks showing on the fabric.

ANIONIC DYES

The suitability of anionic dyes for application to polyamide fibres has been examined. Occasionally, difficulties arise with regard to dye solubility when full depths are desired. However, the use of padding liquor temperatures as high as 50–60°C helps in this respect. If solubility problems persist, the use of solubilising agents, e.g. thiodiglycol and thiourea, is recommended. For certain constructions of fabric made from polyamide fibres, swelling agents, e.g. phenol and benzyl alcohol, are often incorporated in the padding liquor. The use of such agents increases the rate of dyeing by increasing fibre accessibility and often causes tailing problems. These can, however, be overcome by using a two-phase coacervate system. Such a technique, originally developed for the continuous dyeing of wool by a pad–steam process, employing Cibaphasol C or AS [16] (CIBA), can be used to advantage in the continuous dyeing of polyamide fibres with wool dyes. The dye molecules are contained wholly in the coacervate phase and thus are coated over the fibre surface. Diffusion into the fibre from the coacervate phase occurs only under the influence of heat during thermofixation.

REACTIVE DYES

When a thermofixation treatment forms an integral part of a continuous dyeing system for fabrics made from blends of cellulosic and synthetic-polymer fibres, it is possible to apply the dyes for the cellulosic fibre from the padding liquor that contains the disperse dyes for the synthetic-polymer fibre. In this connection both vat [6, 9, 10, 14, 15, 17–19] and reactive [9, 10, 17, 20] dyes have been considered. Mention has already been made of the use of vat dyes on synthetic-polymer fibres, but when they are required to dye the cellulosic component of the blends, an additional reduction–oxidation sequence is necessary. Reactive dyes,

on the other hand, can be fixed on the cellulosic fibres by the same thermofixation treatment which fixes the disperse dyes. When reactive dyes are used, solubility and substantivity are the major factors to be considered. The incorporation of urea in reactive-dye padding liquors considerably increases the solubility of the dye, and since urea is also normally a constituent of disperse-dye padding liquors (to increase colour yields), no problems of solubility should be encountered in mixed padding liquors. With regard to substantivity, most manufacturers of reactive dyes market a range of dyes of sufficiently low substantivity to cellulosic fibres to be applicable by padding.

Application Conditions for Synthetic-polymer Fibres

Initially, an investigation was made into the behaviour of the more frequently used fibres under thermofixation conditions. The results are summarised in Table I.

TABLE I

Effect of Thermofixation Conditions on Man-made Fibres

Fibre	Max. temp. (°C) at which fibre is unaffected by treatment for time of	
	20 s	60 s
Secondary acetate	Unsuitable*	Unsuitable*
Triacetate, e.g. Tricel	220	210
Polyamide, e.g. nylon 6.6	210	200
Polyester, e.g. Terylene	220	220
Acrylic		
Courtelle	170	160
Acrilan	180	170

*Delustring and fibre modification begin at about 90°C.

With this background, application conditions can now be discussed in detail. In the recipes given below, the quantities of thickening agent recommended are for thickeners of the sodium alginate type. In many cases other types may be used, but the quantities may differ from those given.

CELLULOSE TRIACETATE

Fast dyeings have been produced on Tricel (BrC) without any of the listing, ending, or creasing problems often encountered in batchwise processing, using the more slowly diffusing disperse dyes. A typical pad-liquor contains—

	(g/l.)
disperse dye	x
urea	50
thickening agent (Manutex LN)	3–5
Cibaphasol C	1

Urea is included because it increases the rate of fixation of the dyes. The presence of a thickening agent is generally necessary when hydrophobic fibres are being processed, since very little penetration of dye into the fibre occurs in padding, and dye is adsorbed on the fibre surface mainly by mechanical adhesion. For fabrics comprised wholly of synthetic-polymer fibres, most thickening agents are suitable, provided that their thermal decomposition products are easily removed from the fabric by washing. Otherwise, dark brown discolorations will appear at about 200°C. Cibaphasol C is included as a wetting agent to ensure that all available interstices are filled with dye liquor. In certain instances, the dispersing agents present in the commercial forms of disperse dye are adequate for wetting. Excess of surfactant is undesirable because foaming may occur.

Two methods of fixation gave satisfactory results in laboratory trials, viz—

(1) pad–dry–bake

(2) pad–bake.

Method 1 is the conventional pad–thermofix technique. However, investigations have shown that it may be possible to eliminate the separate drying stage and combine drying and fixation. In such a technique, heat transfer must occur at the same rate on both faces of the fabric. Typical conditions would be—

(1) pad; dry for 45 s at 100°C; bake for 45 s at 180°C

(2) pad; bake for 60 s at 180°C.

Both methods have also been used successfully on other fibres and blends.

A wide range of colours has been obtained with combinations of Cibacet (CIBA) dyes of the following C.I. Numbers, as their micro disperse forms—

C.I. Disperse Yellow 3, 12, 42
Orange 20, 38
Brown 1
Red 11, 55, 56
Violet 8
Blue 16, 19, 54, 55

NYLON

The major problems to overcome in dyeing this fibre are (*a*) the tendency for the fibre to become discoloured during thermofixation and (*b*) mechanical problems in padding and in obtaining sufficient liquor pick-up. This is particularly noticeable with the very closely woven 4-oz overall fabric.

Yellowing of nylon fibres by heat can be minimised by restricting the thermofixation temperatures to 180°C, with times varying from 60 to 90 s. The mechanical problems have not been so easy to overcome. The most satisfactory dyes, from the point of fastness, are 1:2 metal-complex dyes and milling acid dyes. The difficulty in applying them arises from their lack of solubility. Synthetic-polymer fibres absorb very little water and hence the only adhesion is in the fibre interstices and on the fabric surface. Under such circumstances, it is very difficult to get sufficient dye absorbed into the fibre to produce heavy dyeings. A technique that has shown great promise makes use of swelling agents for the fibre, e.g. phenol and benzyl alcohol. Dyeings free from tailing can also be obtained by a two-phase coacervate system.

With anionic dyes, suitable pad-liquors would be as follows—

	Non-coacervate (g/l.)	Coacervate (g/l.)
dye	*x*	*x*
thickener (Manutex LN)	3–5	3–5
phenol	10–20	10–20
Cibaphasol C	1	40

Almost all the Cibalan (CIBA) (1:2 metal-complex) dyes have been successfully applied to nylon by thermofixation, as have certain Alizarine Fast and Benzyl Fast (CIBA) acid dyes, where particular colours were required. Suitable dyes are listed by *Colour Index* Number (where applicable) below.

C.I. Acid Yellow 116, 127, 128
Orange 88
Brown 19, 21, 224, 225
Red 106*, 129*, 209, 211, 213, 252, 253
Violet 68, 70
Blue 62†, 129†, 168, 170, 171, 183, 184
Green 25†, 43, 56
Black 60, 62, 107
Cibalan Blue FBL
Cibalan Brilliant Blue RL

* Benzyl Fast dyes.
† Alizarine Fast dyes.

The use of phenol as a swelling agent does not lower the tensile strength of the nylon fabric. Samples of 4-oz filament nylon overall fabric were subjected to various thermofixation treatments, with the results shown in Table II.

TABLE II

	Treatment	Breaking load (lb/in²)	Extension at break (%)
(1)	None	321	40
(2)	Baked for 90 s at 180°C	333	41
(3)	Padded with non-coacervate liquor, baked for 90 s at 180°C	334	43
(4)	Padded with coacervate liquor, baked for 90 s at 180°C	343	44

Despite their somewhat lower fastness properties, disperse dyes can be used for dyeing nylon by the thermofixation method, using the same type of padding liquor as already described for Tricel. Suitable Cibacet dyes (referred to by *Colour Index* Number) in micro disperse form are—

C.I. Disperse Yellow 3
Orange 20, 21, 38
Red 11, 12, 17, 55
Blue 7, 16, 55

POLYESTER FIBRE

Terylene polyester fibre is ideally suitable for dyeing by the pad–thermofix system. No signs of fibre discoloration or degradation have been noted even at temperatures as high as 220°C. Furthermore, a wide range of colours is obtainable, in all depths. It is for this reason that most research work on thermofixation has been concerned with the application of the process to polyester fibre. The major limitation is the sublimation fastness of the disperse dyes, but by careful selection suitable dyes can be found. The fibre is best dyed from a pad-liquor containing—

	(g/l.)
disperse dye	*x*
urea	50
thickening agent (Manutex LO or LN)	3–5
Cibaphasol C	1

Thermofixation conditions may vary from 60 s at 200°C to 20 s at 220°C.

The following Terasil (CIBA) disperse dyes, in micro disperse form, have proved suitable for application to Terylene by thermofixation—

C.I. Disperse Yellow 42, 51, 65
Orange 20, 38
Brown 1
Red 11, 55, 56, 86
Violet 8
Blue 16, 54, 55
Terasil Navy Blue GRL
Black B (as a grey), SL

ACRYLIC FIBRES

Both regular Acrilan (Chemstrand) and Courtelle (Courtaulds) have been dyed successfully by the pad–thermofix process. However, the tendency of these fibres to become discoloured by heat is such that the fixation temperatures have to be kept as low as 170–180°C. Even then, the time spent in the hot zone should be no more than 60 s. Under these conditions, medium to full depths are not attainable and the process is still under development. A suitable pad-liquor would contain—

	(g/l.)
disperse dye	*x*
urea	50
thickening agent (Manutex LN)	3–5
Cibaphasol C	1

Disperse dyes that have been used successfully include Cibacet dyes, in micro disperse form, of *Colour Index* Number—

C.I. Disperse Yellow 3
Orange 20
Red 11, 12, 56
Violet 8
Blue 7, 16, 55

Investigations have been made of the application of basic, e.g. Deorlene Fast (CIBA), dyes to acrylic fibres by this process. Although interesting results have been obtained, especially in the presence of emulsifying agents, e.g. Emulsifier OC (CIBA Clayton), much work remains to be done.

Application Conditions for Blends

POLYESTER–CELLULOSIC FIBRE BLENDS

The method has been successfully used to dye a wide range of these blends, e.g. polyester–cotton, polyester–viscose rayon, and polyester–polynosic fibre, e.g. Vincel (Courtaulds). The simplest

method of producing solid or cross-dyed effects consists in applying the dyes for both types of fibre from the same pad-liquor. If disperse and reactive dyes are used, a single thermofixation treatment will give complete dye fixation on both fibres [9, 10, 17, 20].

The following pad-liquor has been found satisfactory—

	(g/l.)
disperse dye	*x*
reactive dye	*y*
thickening agent (Manutex LN)	3–5
urea	50–200
soda ash	20
Cibaphasol C	1

Thermofixation for 60 s at 200–210°C gives excellent results with dyeings of up to medium depth. Full depths are rather difficult to obtain and are uneconomic to produce by this method.

For pale depths, selected vat dyes have been used with some success to dye both fibres of the blend. Their application has been described by Müller [14] and Musshoff [15], with reference to the Polyestren (CFM) range. Examples of the use of vat dyes in this way have also been described by other workers [6, 7, 9, 10, 17–19]. Only a limited number of vat dyes exhibit the same depth and tone on both constituent fibres. Selected vat dyes may also be used in conjunction with disperse dyes to obtain full depths on these blends. Dyeing of the polyester component by vat dyes during thermofixation may be minimised by careful selection of dyes and by using a fixation temperature of about 190°C, since vat dyes have a fairly low rate of diffusion into polyester fibres at this temperature. At the lower temperature there is a decrease in the fixation of disperse dye, but the greater ease of colour matching under these conditions makes the process more practical. A typical pad-liquor for a mixture of disperse and vat dyes would be—

	(g/l.)
disperse dye	*x*
vat dye	*y*
urea	50
thickening agent (Manutex LN)	5
Cibaphasol C	1

In this case, after thermofixation the vat dye is developed on the cellulosic fibres either on the jig or by pad–steam treatment. The latter is preferable if the necessary equipment is available since the process is then fully continuous.

Experiments have been carried out on the pad–steam development of vat dyes on the cotton component of a Terylene–cotton blend fabric after thermofixation. It has been found that when vat dyes have been pigment-padded, along with disperse dyes, on such a fabric, thermofixation renders their pad–steam development on the cotton more difficult. Some vat dyes subjected to dry heat show dulling on the cotton when developed under normal steaming conditions (20–40 s at 102–105°C) and others, particularly in full depths, give "specky" dyeings. These results suggest that aggregation of vat dyes can take place under thermofixation conditions. At steaming temperatures above 107°C such defects are greatly diminished. A similar improvement is obtained by development on the jig, where the longer period spent under reducing conditions enables disaggregation to take place before fixation is complete.

Many modifications are possible to the scheme for dyeing polyester–cellulosic-fibre fabrics. In some mills only the polyester component is dyed by the thermofixation process and the cellulosic portion is then dyed on a winch or beam; this is particularly useful where full depths are required. The fastness obtainable with selected direct dyes of the Chlorantine Fast (CIBA) type, particularly when the dyeing is aftertreated with a resin, is often satisfactory.

For blends containing either viscose rayon or a polynosic fibre, the general method needs to be modified, if full depths are to be obtained with mixtures of disperse and reactive dyes. Immediately after padding, the fabric is batched cold to enable complete swelling and penetration of the cellulosic fibre to occur. To enable dye to diffuse into the fibre, at least 2 h should elapse before drying and fixation take place. This introduces the problem of dye migration, which can be counteracted by increasing the amount of thickening agent in the pad-liquor. Batching also overcomes the problem of "frostiness", often prevalent in fabrics containing viscose rayon; if the fully continuous thermofixation process without batching is used, undyed viscose rayon fibres are apparent on the fabric surface, but in batching dye diffuses into the undyed surface fibres, giving a much more solid appearance.

Terasil disperse dyes in micro disperse form that have been found suitable for dyeing the polyester component of these blends, from a pad-liquor containing either reactive dyes and alkali or vat pigments, are as follows—

C.I. Disperse Yellow 42, 51, 65
Orange 20, 38
Brown 1
Red 11, 56, 86
Violet 8
Blue 16, 54, 55
Terasil Navy Blue GRL
Black B (as a grey), SL

Suitable Cibacron (CIBA) reactive dyes are—

C.I. Reactive Yellow 2, 6
Orange 5
Brown 2
Red 4, 12, 15, 16
Violet 2
Blue 2, 5, 13, 14, 15
Black 1
Cibacron Golden Yellow 2R–A
Brilliant Green C4G–A

Examples of Cibanone (CIBA) and Ciba (CIBA) vat dyes that will give solid pale dyeings by, e.g. pad–thermofix/pad–steam methods, are—

C.I. Vat Yellow 4
Orange 1, 5*, 9
Brown 3
Red 1*, 35
Violet 2*
Green 30
Black 25, 27

* These are Ciba (indigoid vat) dyes; the rest are Cibanone (anthraquinonoid vat) dyes.

Used in conjunction with disperse dyes, in their micro disperse powder or granular form, the following Cibanone vat dyes, which stain polyesters very slightly, may be used to produce full, solid or cross-dyed effects on polyester–cotton fabrics—

C.I. Vat Yellow 14, 33
Orange 11, 15
Brown 32, 33
Red 10, 24, 49
Violet 1
Blue 6, 14, 18
Green 1, 3, 8, 28, 29
Black 7, 30, 33
Cibanone Brown FBG

POLYESTER–TRIACETATE FIBRE BLENDS

This blend (e.g. Terylene–Tricel) has proved particularly difficult to dye by exhaustion dyeing, since only one class of dye can be used, *i.e.* disperse dyes. Each dye is partitioned in a specific way between the component fibres, owing to the different substantivities. Padding ensures uniform initial distribution of dye through the gross structure of the material and thermofixation conditions increase the rate of diffusion of the dyes into the fibres to such an extent that the opportunities for selective dyeing are considerably decreased.

The following pad-liquor has been used successfully—

	(g/l.)
disperse dye	*x*
thickening agent (Manutex LO)	3–5
Cibaphasol C	1

Optimum thermofixation conditions are 60 s at 190°C. Under these conditions, the Terasil micro disperse dyes found to give satisfactory results were—

C.I. Disperse Yellow 42, 51
Orange 20, 21
Brown 1
Red 11, 55
Blue 54, 55

POLYESTER–PROTEIN FIBRE BLENDS

It is possible to dye the polyester component of a blend such as Terylene–wool with disperse dyes, using the thermofixation method, and then to dye the wool with 1:2 metal-complex or acid dyes in the usual way [20].

A typical pad-liquor would contain—

	(g/l.)
disperse dye	*x*
Imprifix H (carboxymethylcellulose; Kalle & Co.)	8
acetic acid (40%)	2 (ml)
Cibaphasol C	1

After padding and drying, thermofixation for 60 s at 200–210°C fixes the dye on the polyester fibres, without any marked adverse effect on the wool. The disperse dyes may be selected from those already described as being suitable for polyester fabrics (p. 317).

TRIACETATE–CELLULOSIC FIBRE BLENDS

With this blend (e.g. Tricel–viscose rayon), the major difficulty again lies in the coverage of surface rayon fibres. Batching immediately after padding, as described for polyester–cellulosic fibre blends (p. 318), overcomes the problem. The following pad-liquor is suitable for the production of solid or cross-dyed effects—

	(g/l.)
disperse dye	*x*
reactive dye	*y*
thickening agent (Manutex LO)	5–10
urea	50–200
soda ash	20
Cibaphasol C	1

Optimum fixation conditions are 60 s at 190°C. The following Cibacet disperse dyes, in micro disperse form, are suitable for application by this method—

C.I. Disperse Yellow 3, 12, 42
Orange 20, 38
Brown 1
Red 11, 56
Violet 8
Blue 16, 19, 54, 55

Reactive dyes may be selected from those already listed for polyester–cellulosic fibre blends (p. 318).

POLYAMIDE–CELLULOSIC FIBRE BLENDS

Solid and cross-dyed effects may be produced on these blends, e.g. nylon–cotton, nylon–viscose rayon, with mixtures of disperse and reactive dyes from a pad-liquor of composition—

	(g/l.)
disperse dye	*x*
reactive dye	*y*
thickening agent (Manutex LN)	3–5
urea	50–200
soda ash	20
Cibaphasol C	1

Because of the tendency for the polyamide fibre to discolour on baking, the thermofixation conditions should range between 60 s at 180°C and 20 s at 200°C. When viscose rayon is a component of the blend, batching for 2 h is again essential.

Suitable micro disperse Cibacet disperse dyes for the nylon component of these blends are—

C.I. Disperse Yellow 3
Orange 20, 21, 38
Red 11, 12, 17
Blue 7, 16, 55

The reactive dyes that are suitable for use on polyester–cellulose blends (p. 318) may also be used in this case. Full, fast dyeings can also be produced by a combined thermofixation–"acid shock" method [21, 22], using 1 : 2 metal-complex or acid dyes and reactive dyes. A typical pad-liquor would contain—

	(g/l.)
1 : 2 metal-complex or acid dye	*x*
reactive dye	*y*
thickening agent (Manutex LN)	3–5
urea	50
soda ash	20
Cibaphasol C	1

Thermofixation conditions ranging between 5 min at 140°C and 20 s at 200°C fix the reactive dye on the cellulosic fibres and promote diffusion of the anionic dyes into the polyamide fibres. Because of the alkaline conditions, fixation of the anionic dyes does not occur during baking. This is achieved subsequently by passing the fabric over a period of 1–5 min through a boiling solution of formic acid (85%) (3–5 ml/l.), the acid concentration and duration of treatment depending on the depth of the dyeing. The 1 : 2 metal-complex and acid dyes already mentioned as suitable for dyeing polyamide fabrics (p. 317) and the reactive dyes applicable to polyester–cellulosic fibre blends (p. 318) can be used.

ACRYLIC–CELLULOSIC FIBRE BLENDS

Disperse and reactive dyes can be used to give pale- to medium-depth dyeings on, e.g. Acrilan–cotton blends, from a pad-liquor of the same composition as that used for nylon–cotton blends (p. 319). Thermofixation conditions, as with all fabrics containing acrylic fibres, should not exceed 1 min at 170–180°C. Suitable disperse dyes are those already listed for acrylic-fibre fabrics (p. 317), and suitable reactive dyes are those applicable to polyester–cellulosic fibre blends (p. 318).

Interest has been shown recently in the application of mixtures of basic and reactive dyes to these blend fabrics by thermofixation. Medium- to full-depth dyeings, in solid colours and cross-dyed effects, have been obtained using selected basic dyes in the following pad-liquor—

	(g/l.)
basic dye	*x*
reactive dye	*y*
urea	100
soda ash	20
Emulsifier OC	10

Thermofixation is again for 60 s at 170–180°C. The basic dyes used so far have been—

Deorlene Fast Yellow 4RL
Deorlene Fast Red CBL
Deorlene Fast Blue BL

The usual selection of reactive dyes is again available.

Dyeing of Narrow Fabrics

Much interest has recently been shown in the pad–thermofix application of dyes to various kinds of narrow fabrics, i.e. fabrics less than 6-in. wide. In general, narrow fabrics are very suitable for continuous pad–thermofix dyeing, for several reasons, viz.—

(*a*) Suitable machinery is readily available.

(*b*) The length-to-weight ratio is much greater for most types of narrow fabrics than for wider materials. Thus, for the same weight of fabric, far greater lengths have to be dyed and hence continuity of process is ideal.

(*c*) Continuous dyeing processes entail less handling, e.g. in hanking and reeling, than do conventional batchwise methods.

(*d*) In many cases, it is possible to eliminate preliminary batchwise scouring in hank form. Although thorough and even penetration at the padding stage is essential in any continuous dyeing process, the required degree of wetting-out can often be achieved by padding the fabric through a solution of a wetting agent and then drying it before padding with dye-liquor.

(*e*) Colours are more easily maintained to a standard during a continuous run than they are from batch to batch in conventional hank dyeing.

Typical of machinery specifically designed for the continuous dyeing of narrow fabrics are the units made by Breitenbach Bandfabrik A.G. and Ernst Benz A.G., both of Switzerland. Other manufacturers also supply suitable equipment, but rather more experience has been gained of the methods of operation of these two types.

The Breitenbach system utilises infrared radiation as a means of achieving drying and thermofixation and is so controlled that overheating and scorching are virtually impossible. In the Benz equipment, hot air at predetermined temperatures is used to achieve drying and thermofixation, in either small nozzle-type dryers or roller-flue bakers. Whatever system is used, the initial application of dyes by padding ensures levelness and the subsequent thermofixation treatment may be controlled to give full penetration and fixation.

Narrow fabrics composed of Tricel, nylon, Terylene, nylon–cotton, and nylon–viscose rayon have all been dyed successfully by this method. In general, the techniques used are the same as those already discussed for similar full-width fabrics, but a few specific comments may be of interest. For example, with Tricel ribbon, it was found that, unless heat-setting was carried out before padding, lack of dimensional stability led to curling of the edges. As with many synthetic-polymer fibres, heat-setting before dyeing reduced the substantivity, but this could be partially compensated by padding with a solution of a wetting agent and drying beforehand, this process leading to a higher colour yield. A distinct advantage of the pad–thermofix method is that disperse dyes of larger molecular size, slower diffusion rates, and higher fastness can be used satisfactorily, whereas in exhaust dyeing they would give rise to serious

levelling problems even if there were only slight variations in temperature.

The recent demand for motor-car safety-harness webbings made from filament nylon or Terylene has also aroused considerable interest in thermofixation. Batchwise dyeing gives rise to considerable penetration difficulties, and dyeing of yarn before weaving was originally thought to be the best solution. This has the disadvantage that the manufacturer would have to carry large stocks of yarn dyed to a fairly limited range of colours. Clearly, dyeing of the woven fabric would offer greater flexibility and a wider choice of colours. Pad–thermofix methods, using disperse dyes on Terylene, and disperse and anionic dyes on nylon, have proved satisfactory, giving level dyeings and good penetration. The only basic difference in dyeing techniques from those already described will arise with very tightly woven webbings, where it may be necessary to increase the amount of wetting agent in the pad-liquor to assist dye pick-up and penetration.

Application of Resin-bonded Pigments

The advantages of a padding system containing a pigment dispersion and resin–binder emulsion are that the method of application is the same for all substrates. This enables solid dyeings to be obtained easily on blends. Consideration must, however, be given to the curing treatment, which is necessary to polymerise the resin, and its effect on the material being processed.

There are no substantivity effects, so that there is no occurrence of "tailing" or preferential pick-up of dye in certain areas because of chemical or physical differences within the substrate. The aspects of padding, drying, and curing (thermofixation) already described apply equally to this technique, and as an example the Microfix (CIBA) method will be described. The pad-liquor contains the Microfix pigment, a binder, a catalyst, and water. The sequence of operations is pad, dry, and bake to polymerise the resin.

The binder is an essential part of the process and two are available. Binder 59 (CIBA) gives good pigment fixation on natural and synthetic-polymer fibres and on blends. A newer product, Binder PE (CIBA), has advantages when used on polyesters, giving a high degree of fastness to rubbing, wet scrubbing, and solvents.

The limiting factor in pigment systems is the depth attainable. Pale to medium depths can be obtained in very high fastness, but the rubbing fastness of full-depth dyeings is less satisfactory.

The following composition would be suitable for the pad-liquor—

	(g/l.)
Microfix pigment	*x*
Microfix Binder PE	10–80
sodium alginate (Manutex RS)	1
diammonium hydrogen phosphate	5

After padding and drying, resin curing should take place under any of the following conditions of time and temperature—

Time (s)	Temperature (°C)
300	140
240	150
180	160
90	170
60	180
30	190
15	200

The amount of Binder PE used depends on the depth desired, ranging from 20 g/l. at 1/50 standard depth, through 40 g/l. at 1/25, to 80 g/l. at 1/12 standard depth, which is the maximum attainable.

After the baking stage, washing off is unnecessary, but calendering may improve the handle of the material. Certain finishes can be applied from the same pad-liquor as the pigment, provided that they are anionic or non-ionic in character.

Fig. 9 shows the solidity of the coloration obtained when Microfix pigments are applied to various blends and also illustrates the similarity in hue between the various blends for the same Microfix pigment.

* * *

We thank those of our colleagues, particularly Mr. T. Green, who have assisted in the preparation of this paper.

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(*MS. received 18th October 1963*)

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DISCUSSION

Mr. R. K. FOURNESS: Firstly, in using the thermofixation process with disperse dyes, has any breakdown of the dispersion been experienced, resulting in the formation of dye specks? Would the use of paste forms of disperse dyes, as in printing, be advantageous?

Secondly, how do the fastness properties of thermofixation dyeings compare with those of

conventionally dyed fabrics? In particular, is it possible to obtain higher wet-fastness properties on cellulose triacetate fabrics by thermofixation dyeing methods?

Mr. KEATON: In general, the quality of dispersion obtainable from disperse dyes, in their modern physical forms, is adequate for the continuous operation of the thermofixation process. Paste brands sometimes tend to settle and dry out in storage, giving heterogeneous dispersions.

With reference to fastness properties, at least equivalent, and sometimes superior, results are obtainable by thermofixation. Cross-sections of fibres dyed by conventional exhaust, pad–thermofix, and Pad–Roll methods have shown that complete penetration is obtainable by both exhaust and thermofixation dyeing. Some Pad–Roll dyeings show evidence of ring-dyeing. The wet-fastness properties of dyeings on triacetate can be improved by using the pad–thermofix process or by giving a short thermofixation treatment after exhaust dyeing.

Mr. H. BELLIS: Are full depths obtainable by the pad–thermofix process?

Mr. KEATON: Examples from bulk working have shown that it is perfectly feasible to dye all depths on synthetic-polymer fibres by this method.

Dr. G. T. DOUGLAS: When phenol is used in padding liquors for the thermofixation dyeing of nylon, has any difficulty been found in its subsequent removal from the dyed fabric?

Mr. PRESTON: If the final washing-off treatment, an essential part of all continuous processes if maximum fastness properties are required, is sufficiently vigorous to remove all unfixed dye, thickener, and other assistants, then this has always proved to be completely effective in removing all traces of the phenol.

COMMUNICATIONS

The Sorption of Acids by Wool from Mixtures of Acids
IV—The Sorption of Orange II Dye Acid from Mixtures with Hydrochloric Acid and with Trichloroacetic Acid*

P. LAROSE and R. DONOVAN

The amounts of Orange II dye (C.I. 15510) sorbed from solutions containing mixtures of the dye acid or the sodium salt of the dye with hydrochloric acid or with trichloroacetic acid were measured. The results show that, although the sorption of hydrochloric acid or trichloroacetic acid from the mixtures is normal, the sorption of the dye acid is anomalous and quite different from that of the acids studied earlier. Competition between the dye anion and the counteranions is overshadowed by a secondary effect which results in an increase in the amount of dye sorbed as the concentration of the counterion is increased. A possible explanation for this effect is suggested.

Introduction

In previous communications [1], we showed that, in mixtures of hydrochloric acid with acetic acid and with the three chloro-substituted acetic acids, there was a definite relation between the relative amounts of the anions sorbed by wool and their concentrations in the solution with which the wool was in equilibrium. Since the mechanism of acid-dye sorption is generally regarded as similar to that which is used to explain the sorption of the simpler acids, such as those investigated in our earlier work, it seemed desirable to carry out tests with mixtures of acids in which a dye acid was one of the components. We have chosen to work with Orange II (C.I. 15510), since this dye has already been widely used in sorption measurements and because it is easily purified. The dye acid (in some cases its sodium salt) was used in mixtures with hydrochloric acid and with trichloroacetic acid.

Experimental

The sodium salt of the dye was purified by the method of Robinson and Mills [2]. The dye acid was prepared from the purified salt by passing a solution of the dye through a column of Amberlite IR 120 resin in the acid form. The purity of the acid dye was checked in various ways. A known weight of the dried material was used to prepare a standard solution, which was then analysed by titration with standard ceric sulphate in the presence of an excess of sulphuric acid [3] and with a ferroin indicator. We found that the addition of the indicator makes the change in colour sharper and gives more accurate results than does reliance simply on the change of colour of the dye solution itself. The acidity of the solution was also measured by titration with standard alkali, and the titer of the solution was determined by colorimetric measurements and comparison with the colour of standard solutions of the sodium salt. All these measurements agreed within less than 2%.

The solutions in equilibrium with wool were titrated with standard alkali to determine total acidity. The amount of dye remaining in the solution was determined colorimetrically and the chloride ion concentration was measured by electrometric titration with standard silver nitrate solution. In the experiments where trichloroacetic acid was used instead of hydrochloric acid, the concentration of the trichloroacetate ion was taken as the difference between the total acidity and the concentration of the dye anion. Otherwise the procedure was that followed in our earlier experiments, except that the time of immersion was much longer, namely five days at room

* Issued as National Research Council No. 7950.