

Dyeing Behavior of Polypropylene Blend Fiber. II. Ionic Exchange Mechanism of Dyeing

JIŘÍ AKRMAN,* JOSEF PŘIKRYL

Department of Textile Chemistry and Fibres, University of Pardubice, CZ 532 10, Pardubice, The Czech Republic

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ABSTRACT: The dyeability of polypropylene fibres modified by two nitrogen polymeric additives containing dye sites of different basicity and accessibility was investigated using an acid dye. The thermodynamic and kinetic parameters of dyeing under infinite bath conditions were determined for four aqueous dye solutions. It is postulated that ionized molecules of acid dyes diffuse within the fiber after activation of a dye site by a suitable agent. In addition, color yield and color fastness of various dyes have also been studied. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 543–550, 1997

Key words: polypropylene fiber; dyeing; additive; ionic exchange; color fastness

INTRODUCTION

A great amount of research effort has been expended on making polypropylene dyeable, because good dyeability is essential for widespread commercial acceptance of any textile fiber, and unmodified polypropylene can be considered undyeable for all practical purposes due to its paraffinic nonpolar structure. The problem of increased dyeability of polypropylene fibers was discussed in detail by M. Ahmed in Chap. X of his book.¹ The efforts to introduce dye receptor sites into polypropylene fall into three general groups: (1) copolymerization, (2) chemical modification, and (3) additives.

Copolymerization is difficult with polypropylene because the Ziegler–Natta-type catalyst systems are not effective in the presence of highly polar monomers. The products obtained are not suitable for fiber preparation. Graft copolymerization and chemical modification of polypropylene in various ways has also been suggested. A process of this sort, however, tends to take place on the

surface, only being accompanied by extensive degradation including crosslinking. Attempts at graft copolymerization and chemical treatment are predestined to fail due to their poor reproducibility and high cost. Only corona discharge, as a treatment process for polyolefin films to make them susceptible to printing and coating, has reached some commercial success.

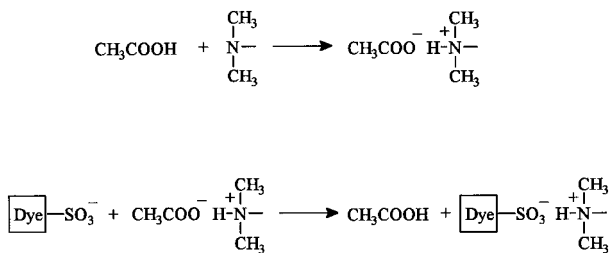
The bulk of the effort on dyeability has been to incorporate the dye receptor as an additive, physically blended with the polypropylene. Many types of chemical compounds have been tried and the number of patents issued on this topic reaches the hundreds.¹ A popular dye receptor is organometallic compounds, especially those containing nickel, due to their ability to form chelates between the metal and 1,2-disubstituted dyes. A special class of dyes, the mordant disperse dyes, is required for this dyeing system.

The second main direction of experimental work has been aimed at developing acid-dyeable PP fibers. The possibility of having the same dyeing system for PP fiber, nylon, and wool is attractive. All conceivable polymeric compounds containing nitrogen groups at the chain end or along the molecular chain have been investigated. Examples of such compounds are polyureas, condensation products of epichlorhydrin with amines, copolyamides containing tertiary amine, or piper-

* Present address: Research Institute of Organic Syntheses, CZ 532 18 Pardubice, The Czech Republic.

Correspondence to: J. Přikryl.

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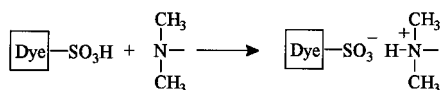


Scheme 1

zine structures along the chain. Polymers with heterocyclic N-groups such as pyridine groups form another important class of compounds extensively investigated for acid dyeability of polypropylene. The most important of this class of additives are the copolymers of ethylene and aminoalkyl-acrylate²⁻⁴ or the copolymers of vinylpyridine with long chain alkyl acrylates.⁵⁻⁷ In general, it has been found that the construction of a basic dye receptor system can be regarded as being governed by two criteria: the basicity of nitrogen, and the minimum amount of nitrogen that must be incorporated into the fiber for dyeability. The more basic the nitrogen, the less is the amount required in the fiber for additives with the same compatibility with polypropylene.

The dyeing of basic modified polypropylene fibers with anionic dyes in aqueous solution is an ion exchange reaction. Before such reaction can take place, the dye must reach the functional group of the additive. It may be assumed that at first the small movable molecules of organic acid used to acidify the dyebath diffuse into the fiber and protonate the dye sites (see Scheme 1). The protonated dye site attracts the dye anion by Coulombic forces. The principle of electroneutrality in the fiber must be preserved. The anion of dye replaces that of acid due to its higher affinity. The anion of the dye has a complex character, and when it is bound on fiber, further kinds of interactions take place together with ionic forces.

The penetration of acid dyes in the form of unionized molecules offers another possibility to explain the dyeing mechanism of acid-dyeable fibers (see Scheme 2). It is true for most acid dyeable polypropylene systems that the dyeability with acid dyes increases with decreasing pH of the dye bath.¹ It is evident that a low pH decreases the



Scheme 2

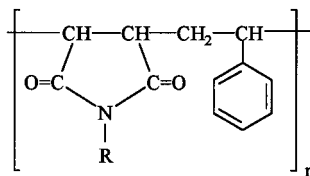
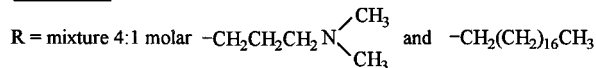
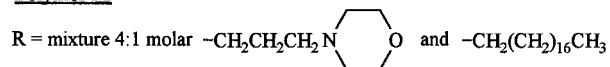
**Polymer A****Polymer M**

Figure 1 Composition of basic polymeric additives.

ionization of dye molecule. According to this postulate, the acid dye may behave as a disperse dye in the undissociated form and may penetrate into the fiber by a polysolution mechanism. This aspect of dye diffusion is supported by the fact that organic acids, such as acetic acid, are better absorbed by acid-dyeable polypropylene fibers than are strongly ionized inorganic acids, such as HCl.⁸

In our previous articles we reported on various aspects of building of color on PP fibers modified by styrene-amine resin.⁹⁻¹¹

It was found that the main driving forces of dyeing are Coulombic interactions. This article provides further experimental evidence about the ion exchange mechanism of dyeing and discusses some practical implications from the point of view of color-fastness properties.

EXPERIMENTAL

Fibers

The PP fiber modified with 6% wt of a styrene-amine resin Polymer A (Fig. 1) was used for the dyeing experiments. Chemically, this is a styrene-maleic anhydride copolymer imidized with a mixture (4 : 1 molar) of 3-dimethylaminopropylamine and octadecylamine. An additive synthesis, its physical parameters and the PP modified fiber preparation were described in Part I¹¹ and in a patent specification.¹² To evaluate the basicity of the dye site, another additive was also synthesized by imidating STY-MA copolymer using a mixture of 3-(4-morpholino)propylamine and octadecylamine in 4 : 1 molar ratio (Polymer M, Fig. 1). This additive, blended with PP powder, was

Table I Dyeing of Polymer A Containing PP Fiber with Acid Orange 7 from Infinite Dyebath

Medium	Saturation Value S [mmol/kg]	Standard Affinity $\Delta\mu^\circ$ [kJ/mol]	Diffusion Coefficient $10^{11}D$ [m ² /s]	Activation Energy ΔE [kJ/mol]
Concentrated acetic buffer	110	-7.04	7.52	42.0
Diluted acetic buffer	84	-11.00	4.74	34.9
Diluted benzoic buffer	110	-9.62	3.05	30.2
Free acid	115	-6.94	0.56	5.0

processed into a fiber at the identical spinning conditions as those for Polymer A containing PP fiber.

Fiber Pretreatment

A part of the fibrous material was pretreated by placing a 20 g fiber sample together with 5 g methyl iodide into a stainless beaker and rolling in dyeing machine for 48 h at 45°C. After that, the sample was dried in air. An attempt was made to follow the degree of quaternization of nitrogen groups by IR spectrometry (KBr disc technique). Broadened bands of water in the spectra have been recorded repeatedly. Samples (5 g) of the fibers were conditioned to 66% relative humidity over a saturated solution of sodium nitrite at 20°C. The weighed samples were then dried in an oven at 110°C for 3 h, and the dry weight was determined. It was found that both Polymer A containing PP fiber and Polymer M containing PP fiber absorb less than 0.2% water. In contrast to that, the methyl iodide pretreatment increased the moisture sorption to the level of 4–5% by weight, while traces of water could not be removed, not even by long-term drying in vacuum.

Dyeing from Infinite Dyebath

The dyeing with C I Acid Orange 7 from an infinite dyebath at 95°C was performed in a concentrated acetate buffer: 0.5M acetic acid + 0.05M sodium acetate, in diluted acetate buffer 0.025M acetic acid + 0.0025M sodium acetate, and in diluted benzoate buffer 0.025M benzoic acid + 0.0025M sodium benzoate. In all the experiments, the acidity was pH = 3.5 (60°C). The saturation value S , and standard affinity of dyeing $\Delta\mu^\circ$, were calculated from the Langmuir sorption isotherm, and the apparent diffusion coefficient D was determined by applying the kinetic data to Hill's equation.¹¹ The activation energy of diffusion (E in the interval of 75–95°C was calculated from the temperature dependence of the diffusion coefficient using the Arrhenius diagram. The values obtained are summarized in Table I. The dyeing was

also carried out with C I Acid Orange 7 free acid without any other chemicals. The free acid of the dye was prepared by precipitation from an aqueous solution of its sodium salt with hydrochloric acid–acetic acid using the method described by H. Delmenico and R. H. Peters.¹³ Measurements of diffusion coefficient were carried out at the concentration of the dye in a bath of 0.25 mmol/L as at this concentration the C I Acid Orange 7 free acid dissolved in distilled water exhibits the same acidity as the buffers.

Dyeing Under Practical Conditions

The dyeing with a finite dyebath (2% depth, liquor ratio 50 : 1) was started at 60°C and pH = 5.0 (acetic acid). A dyeing test apparatus type FE-09 (Metrimpex Budapest) was used in the experiments. The temperature was raised to 100°C during 40 min, the acidity was adjusted at pH = 3.5, and the dyeing was continued for a further 20 min. The material was rinsed with distilled water and washed in 2 g/L sodium laurylsulfate solution

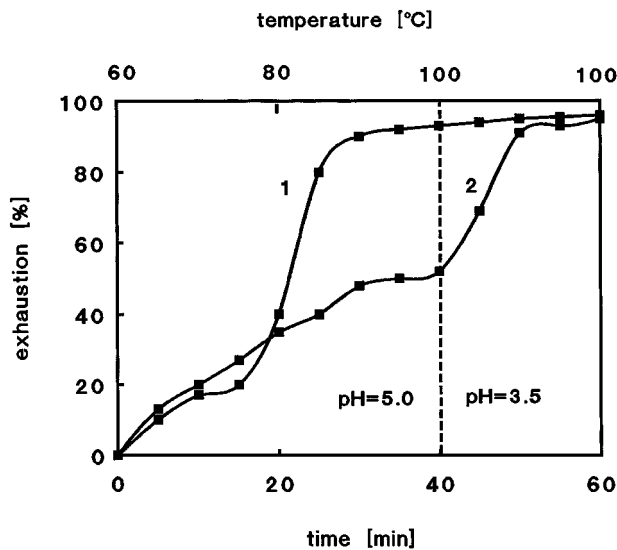


Figure 2 Exhaustion curves of C I Acid Orange 7 (2%) on PP fibers containing Polymer A.

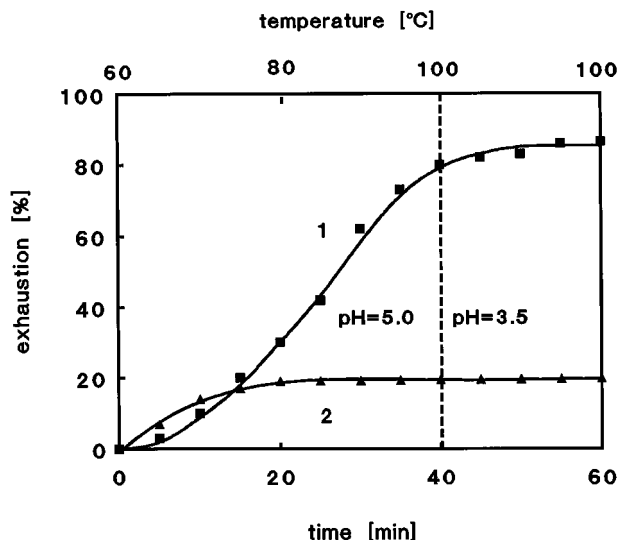


Figure 3 Exhaustion curves of C I Acid Orange 7 (2%) on PP fibers containing Polymer M.

for 20 min at 40°C. After that, it was rinsed with water again and dried at 40°C. The percentage of dye exhaustion and fixation was measured spectrophotometrically by sampling the dyebath before and after the dyeing process and by sampling washing solution and rinsing waters.

The reflectance curves of dyed fabrics were measured with a spectrophotometer Datacolor 3890. The color yield was expressed as the integral value I_v .¹⁴ The dyed fabrics were evaluated for light fastness (Xenotest), wash fastness (60°C), shampooing, crock fastness (dry), and dry cleaning (heavy petrol, 25°C) according to the ISO procedures. The results obtained are summarized in Tables III, IV, and V.

RESULTS AND DISCUSSION

The dyeing of untreated PP fibers containing Polymer A requires both 100°C and strong acidity of the dye bath for complete transport of acid dye from the bath onto the fiber (curve 2 in Fig. 2). On the other hand, the rate of dyeing at these conditions is very high (see the diffusion coefficient of the order of 10^{-11} m²/s in Table I). To obtain a controlled exhaustion and the maximum leveling, it is recommended that the temperature be increased slowly and pH decreased gradually.

The sensitivity to pH was lost after quaternization of a dye site. This is a clear demonstration that the main function of acid in the bath is to "activate" the dyesite on the fiber, and therefore,

the first of the two dyeing schemes proposed seems to operate.

An interesting fact useful in discussing the ion-exchange mechanism of dyeing N-modified PP fibers is obtained from the exhaustion experiments on PP fiber containing Polymer M (Fig. 3). The dye sites on PP fiber containing Polymer M (morpholine groups) are less basic and less accessible than those on PP fiber containing Polymer A (dimethylamino groups). The PP fiber containing Polymer M absorbs the acid dye very badly even at pH = 3.5. However, the quaternization removes differences in basicity and accessibility. Moreover, the conversion of the basic polymer to an ionic complex by reaction with methyl iodide may enable it to absorb water. The resulting increase in dyeability is dramatic and the treated fiber is now highly dyeable.

Dyeing with acid dyes has been commonly carried out from acid aqueous solutions of their sodium salts. However, another procedure also may be used: dyeing using the free sulfonic acid of the dye. In this procedure the dyebath is acidified by the dye itself. The equilibrium isotherm of C I Acid Orange 7 free acid on PP fiber containing Polymer A without any other chemicals may be regarded as a titration curve of fiber with colored acid (Fig. 4).

The thermodynamic and kinetic parameters characterizing free acid dyeing under infinite dyebath conditions are collected in Table I together with the data from the experiments in various buffer media. When the dye bath is composed of free acid alone dissolved in water, the dyeing (Scheme 2) can be predicted to operate. The diffusion coefficient is 13 times lower than that for the concentrated acetate buffer. In other words, an

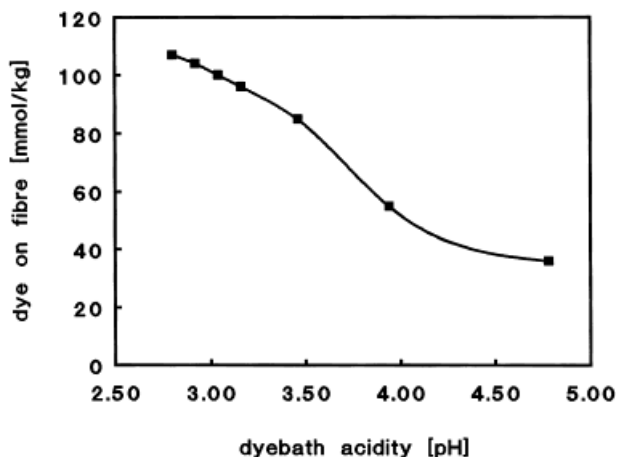


Figure 4 Titration of PP fibers containing Polymer A with C I Acid Orange 7, free acid, 95°C.

Table II Exhaustion of Acid Red 73, 2% o.w.f.

Auxiliaries 2% o.w.f	Exhaustion
None	85%
Sodium sulfate	83%
$C_{12}H_{25}O-SO_3Na$	78%
$C_{12}H_{25}O-(CH_2CH_2O)_4-SO_3Na$	79%
$C_{12}H_{15}O-(CH_2CH_2O)_7-CH_2COONa$	84%
$C_{12}H_{25}O-(CH_2CH_2O)_{10}-H$	85%
$C_{12}H_{25}O-H^a$	79%
Dichlorobenzene ^a	76%
<i>o</i> -Phenylphenol ^a	73%

^a Emulgated by $C_{12}H_{25}O-(CH_2CH_2O)_{10}-H$.

addition of simple organic acid causes a considerable increase in the rate of dyeing. The difference in the values of diffusion coefficients is so great that two different diffusion mechanisms may be assumed to occur.

The thermodynamic quantities of dye sorption also changed. The saturation value decreased and the affinity for dyeing increased in the presence of organic acids. Two phenomena operate simultaneously: the small movable molecules of acid help to open the fiber for a dye and, at the same time, they can be sorbed by basic groups of modified fibers and act as a competitor for dye anions. The lesser ion competition on dye sites in the diluted acetate buffer is reflected by the higher affinity and the lower activation energy in comparison with those in the concentrated buffer. The concentrated acetate buffer, 0.5M CH_3COOH , requires consumption of 30 g acetic acid per 1 liter of dyebath. From the point of view of conditions of practical dyeing in a dyehouse the buffer concentration given seems much too high. That is why the experiments were repeated in a diluted acetate buffer. When the dyeing was performed in a 20 times diluted acetate buffer, the number of accessible dye sites was lowered from 110 to 84 mmol/kg. The experiments were completed by dyeing in benzoate buffer of the same molarity and the same pH as those of the diluted acetate buffer. The buffer requires a bath with doping benzoic acid of about 3 g/L concentration. The diluted benzoate buffer provides a saturation value of 110 mmol/kg. It can be seen that benzoic acid provides the same number of accessible dye sites as acetic acid does, but a 20 times lower molar concentration is needed (Table 1).

Application of a wetting agent is often recommended to make the transfer of dye from aqueous solution into the hydrophobic polymer easier. C I Acid Red 73 exhausted to the extent of 85% with

PP fiber containing Polymer A from 2% o.w.f. dyebath. Nonionic surfactants, such as an oxethylated lauryl alcohol, did not improve the exhaustion. Strongly anionic surfactants, for instance, sulfonated oxethylated lauryl alcohol or lauryl sulfate, even caused a holdup of dye in the bath. This may be a consequence of creation of aggregates between dye and surfactants in solution or blocking of basic dye sites on fiber surface by anionic groups of the surfactants.

Of special importance in the dyeing of hydrophobic synthetic fibers is the use of swelling agents and carriers in the dyebath to render the fiber more permeable to the dye. Movement of swelling agent into the polymer is accompanied by increased polymer chain mobility and more ready diffusion by dye molecules. Some of the auxiliary agents listed in Table II, particularly dichlorobenzene, *o*-phenylphenol, and lauryl alcohol, are known to be efficient in the swelling of polypropylene. However, their presence in the dyebath did not induce the transfer of dye from aqueous solution into the polymer phase. Dichlorobenzene even caused plasticization and damage of the fibrous sample. After the dyeing process, the tubular knitted PP fabric was deformed in shape and rough in the hand. The swelling agent, of course, can also swell additive particles dispersed in fibers besides polypropylene. The polar dye receptor, in contrast to polypropylene, is able to be also swelled by water. Water molecules can compete with the swelling agent in binding on a macromolecular chain of additive. If the dyeing has resulted in a decreased dye uptake as can be seen from Table II, it may be concluded that aqueous pathways are favorable to diffusion, and there-

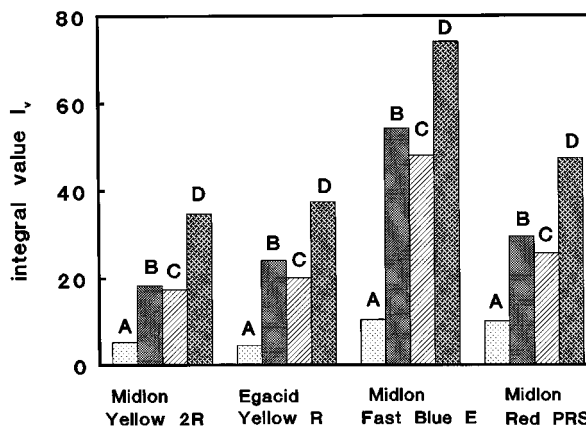


Figure 5 Dependence of color yield on dyebath acid used, PP fibers containing Polymer A: (A) tartaric acid; (B) formic acid; (C) salicylic acid; (D) benzoic acid.

Table III Dyeability of Polymer A containing PP Fiber

Dyes		Formic Acid			Benzoic Acid		
Commercial Name	C.I. Name	Exhaustion	Fixation	Integral Value	Exhaustion	Fixation	Integral Value
Egacid Yellow G	Acid Yellow 11	93%	87%	28.44	98%	92%	33.82
Egacid Yellow T	Acid Yellow 23	99%	93%	52.44	92%	91%	54.41
Midlon Yellow E	Acid Yellow 61	93%	84%	18.70	91%	77%	23.04
Egacid Red MOOL	Acid Red 73	85%	79%	92.23	86%	81%	92.95
Midlon Blue ASR	Acid Blue 145	96%	92%	35.20	97%	92%	37.54
Rybacid Green G	Acid Green 25	99%	83%	45.80	93%	79%	58.45
Midlon Blue B	Acid Blue 78	97%	93%	35.99	94%	86%	42.49
Egacid Blue B	Acid Blue 45	99%	93%	56.08	96%	89%	56.08

fore, the dye molecules diffuse into the fiber in the dissociated rather than undissociated form.

The presence of sodium sulfate did not influence the exhaustion of a dyebath. A salt such as sodium sulfate is usually added to the dyebath to facilitate the dye uptake, notably in the case of natural fibers. It has been postulated that salt can serve a number of purposes. The solubilities of dyes are decreased and this favours "salting out" of dyes onto the fiber. Also, there is a reduction in the osmotic work that must be done when dye ions enter the fiber. A high concentration of counteranions screens any buildup of negative charge on the fiber surface. The polymers with electrically charged groups, such as basic dye polymer receptors, exhibit a zeta potential when in contact with electrolyte solutions in water. We have investigated the streaming potential of modified polypropylene fiber using a silver cell similar A significant positive zeta potential was recorded at low pH. The positive ZP was also measurable after an addition of $10^{-3}M$ Na_2SO_4 and $10^{-3}M$ Acid Orange 7. The positive charge on the fiber surface favors anionic dye adsorption and, therefore, an addition of electrolyte is unnecessary for altering the charge on the fiber surface.

Two important conclusions can be stated from the discussion realized so far about the mechanism of dyeing cationically modified polypropylene fibers: 1) acid dyes diffuse within the fiber in the dissociated form. It may be concluded that penetration does not occur through a layer of non-polar polypropylene. 2) The mechanism of sorption is like that of an ion exchanger. For an ion exchange to take place, the first step, i.e., activation of dye sites on the dye receptor, must occur.

These postulates are supported by some further experiments. The most marked influence between the auxiliary agents added to the bath, on

color strength of dyed fabric, is by the acids. Figure 5 illustrates the effect of tartaric acid, formic acid, salicylic acid, and benzoic acid, respectively, on color strength of four strong acid and milling dyes on PP fabric containing Polymer A. The acids were doped to the dyebath to adjust the acidity at pH = 3.0. The polar tartaric acid is wholly unsuitable. Sulfuric, hydrochloric, and oxalic acids gave similar results—the dyeing was pale and uneven. The most intensive color effect was achieved by using benzoic or formic acid. Salicylic acid gave a lower color strength, although it is claimed⁴ as an auxiliary agent in dyeing of PP fiber modified with copolymer ethylene and basic alkyl acrylate.

We have carried out a detailed study of the action of benzoic acid and formic acid on dyeability and fastness properties of eight acid dyes (Tables III and IV). The exhaustion and fixation was higher for the majority of dyes in the case of benzoic acid. However, first of all, benzoic acid produces deeper shades. In addition, the color strength of certain dyes—Acid Yellow 61, Acid Green 25, Acid Blue 78—is greater even when the fabrics contain a smaller amount of the dye. This finding indicates a difference in distribution of dye in the substrate. It is known that the same amount of coloring matter, when more evenly distributed over the same bulk, gives a more intensive color effect. We observed the cross section of fibers under a light microscope where all samples appeared to be dyed uniformly. Perhaps benzoic acid guarantees a more even spreading of coloring matter over the dispersed additive particles. The color fastness properties support such an idea, as the dyeings with benzoic acid exhibit better fastness particularly to washing and to shampooing. Staining on adjacent fabric also improved. Because a considerable portion of ionic interactions are presumed to exist in the overall bonding of

Table IV Color Fastness Properties of Dyed Polymer A Containing PP Fiber

Dyes	Formic Acid					Benzoic Acid				
	Washing	Shampooing	Rubbing	Petrol	Light	Washing	Shampooing	Rubbing	Petrol	Light
Yellow 11	4/4	4-5/4-5	4-5	4-5	5	4-5/4-5	4-5/4-5	4-5	4-5	4-5
Yellow 23	4/4	4-5/4-5	4-5	4	2-3	4-5/4-5	4-5/4-5	4-5	4	3
Yellow 61	4/4-5	4-5/4-5	4	4	4	4/4-5	4-5/4-5	4-5	4	4
Red 73	4/4-5	4-5/4-5	3-4	4	4	4/4-5	4-5/4-5	4	4-5	3-4
Blue 145	3-4/3-4	3/4-4	3-4	4	3-4	4/4	4-5/4-5	4-5	4-5	3-4
Green 25	2-3/4	4/4-5	4-5	4	4	4/4-5	4-5/4-5	4-5	4-5	4
Blue 78	2-3/4	4/4	4	4	3-4	4/4-5	4-5/4-5	4	4-5	3-4
Blue 45	4/4	4/4	4	4	6	4-5/4-5	4-5/4-5	4-5	4-5	6

dye on fiber, better dry fastness and worse wet fastness may be expected. Actually, the fastness both to rubbing and to dry cleaning is excellent, and the fastness to washing and to shampooing is also very good, notably with benzoic acid.

The dyestuffs listed in Table III were developed and are manufactured for dyeing wool, suggesting one compare the dyeings by the same dye on two different substrates. The brightness and hues of shades obtained on PP fabric are similar to those of identical dyes on wool. The exhaustion is also similar, which makes the potential blending of both fibers attractive in terms of solid dyeing of an intimate blend with one dye in one bath. When comparing the fastness, we can see a difference in resistance to light exposure. The fastness to artificial sunlight, Xenotest, is about two points lower in the case of polypropylene. The causes of decreased light fastness for N-modified PP fibers may be expected from 1) a strong tendency of polypropylene to undergo photooxidative radical degradation, which can be reflected in damage to the chromophore of the dye; 2) absorption by the additive in the UV range of the spectrum; the absorbed energy can be transformed to breaking down chemical bonds; and 3) the basic nature of the nitrogen additive, which can be involved in the dye fading process.

It was found that the light fastness on modified

PP was slightly better when certain photostabilizers were applied in the melt spinning of polypropylene fiber to protect the fiber against deterioration of its physical properties. HALS stabilizers in connection with phosphite esters were particularly efficient in this respect; however, the main way to obtain dyeings resistant to fading lies in searching for potential dyestuffs.¹⁶

A hydrophobic fiber such as modified polypropylene should easily be dyeable with water-insoluble disperse dyes. Results of dyeing of PP fiber containing Polymer A with four commercial disperse dyes are given in Table V. Having compared the results of dyeing in Tables III and V, we can see poorer color fastness of disperse dyeing in all the tests studied. It is apparent that disperse dyes are held on the fiber by weaker forces than anionic dyes. The exhaustion for disperse dyes is lower, too. Evidently, the hydrophobic PP better absorbs polar anionic dyes carrying sulfonic groups.

CONCLUSIONS

An effective way to make polypropylene fibers dyeable is the physical modification of them by basic nitrogen polymeric additives. The dyeing mechanism of these fibers with anionic dyes is like that of an ion exchanger. Thermodynamic and

Table V Dyeing of Polymer A Containing PP Fiber with Disperse Dyes (2%)

Dyes		Dyability	Color Fastness		
Commercial Name	C.I. Name	Exhaustion	Washing	Petrol	Light
Ostacet Yellow SE-LG	Disperse Yellow 42	77%	4	4	2-3
Ostacet Scarlet S-L2G	Disperse Red 54	57%	4	3-4	1-2
Foron Ruby S-2GFL	Disperse Red 167	53%	3-4	3	1
Foron Turquoise S-BL	Disperse Blue 87	43%	2-3	2-3	1-2

kinetic examinations of dyeing parameters and experiments with fibers pretreated with a quaternization agent provide a more detailed picture of the ion exchange process, and the results can be summarized as follows. For a preferential mass transfer of dye from aqueous solution to the polymer phase to take place, three requirements have to be satisfied: 1) the dye site on the additive should be strongly basic and accessible, 2) the temperature and pH of dyebath should be adjusted to the optimum level, and 3) the dye bath should contain a suitable auxiliary agent that is able to activate the dye site on fiber for an ion exchange.

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