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Commercially Adaptable Coloration Processes for Generic Polypropylene Fiber

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1. Introduction

Polypropylene (PP) fibers belong to the newest generation of large-scale, manufactured chemical fibers, having the fourth largest volume in production after polyesters, polyamides and acrylics [1, 2]. PP is one of the most successful commodity fibers, reaching a world production capacity of four million tons a year. Due to its low density (0.9 gm/cc), high crystallinity, high stiffness and excellent chemical/bacterial resistance, isotactic PP is widely used in many industrial applications such as nonwovens, industrial ropes, packaging materials, furnishing products, etc. PP fiber has potential, high-volume applications in the carpet, textile, apparel and industrial textile markets.

Due to its thermoplastic nature, PP fiber is manufactured using conventional melt spinning. Subsequent multistage drawing imparts tensile strength and enhances mechanical properties required for industrial applications. Synthesis of PP polymer involves stereo-regular polymerization of propylene gas using Ziegler-Natta catalysts [3]. Only isotactic polypropylene is useful for fiber applications among the three stereoisomers. Since only a simple monomer, i.e., propylene gas, is involved in the synthesis of PP, this fiber is relatively inexpensive to produce as compared to other high volume textile fibers such as polyesters, acrylics and nylons. The major products of PP fibrous materials are monofilaments, multifilament yarns, staple fibers and yarns, nonwoven textiles (spunbond, meltblown), tapes, split filament, ropes, carpet backing, etc. Crystallinity of isotactic PP is about 70%, and the molecular weight of fiber grade PP is in the range of 80,000 to 300,000 gm/mole. Since the advent of stereo-regular isotactic polypropylene (PP), the fiber has been used in many industrial applications, as well as in carpets and apparel, due to its high degree of crystallinity, good handle, strength and a high enough melting point for normal use. The potential commercial importance of unmodified polypropylene (PP) fiber in the carpet and textile industries has led to research to develop an aqueous dyeing process for the highly-hydrophobic fiber, consistent with the established coloration processes in use for other high-volume fibers (cotton, nylon, polyester and acrylic). Despite substantial research conducted around the globe, a commercially viable and sustainable aqueous dyeing process of PP based on demand-activated manufacturing has not been realized.

PP offers the advantages of exceptionally low price, good strength and aesthetic properties, along with many other desirable characteristics of a textile/carpet fiber, thus creating the

impetus for manufacturing from PP fiber a variety of materials such as towels, floor coverings, sportswear and select technical products. Due to its nonpolar and hydrophobic nature, most of the production of PP fiber is colored by means of mass pigmentation. This route of coloration gives excellent fastness properties during end use; however, it restricts the producer in fulfilling the changing fashion demands of the market. An alternative way of coloring PP fiber exists in which the fiber can be made dyeable by means of post modification, creating active sites for dye association or adding hydrophilic comonomers, but this route has adverse effects on the mechanical properties and costs of the fiber. The development of a truly aqueous process for dyeing PP in its generic, unmodified form is of significant importance vis-à-vis the rising demand for this relatively inexpensive fiber. The developed batch exhaust dyeing methods for PP fiber by us were reported earlier [4-6] and the continuous pad steam and pad/dry heat methods are reported in our recent paper [7]. This chapter covers the state of the art in PP dyeing as well as our adopted approach to develop a commercially viable coloration process for unmodified PP fiber in conventional aqueous systems.

2. Coloration of PP fiber

The major portion of colored PP fibers is currently manufactured by melt pigmentation (called spun dyed fibers) [8]. Melt pigmentation involves the addition of pigment particles in the polymer melt prior to extrusion and fiber spinning. Melt pigmentation can be performed in various ways. Pigments can be added to the pre-melted fiber polymer, or it can be mixed with the chips (also known as chip pigmentation) in order to produce melt pigmented PP fibers.

2.1 Different methods to aqueous dye PP fiber

Three general approaches to aqueous color PP fiber are reported in the literature [9]:
a.   Attempts to color unmodified PP fiber with modified dyeing methods.
b.   Modification of the fiber surface to create dye receptive sites.
c.   Copolymerization and graft copolymerization.
The influence of dyestuff constitution and auxiliaries in the dyeing of unmodified PP has been studied by Herlinger et al.[10] The authors determined that the use of toluene and p-xylene as carriers, together with some anthraquinone disperse dyes having longer alkyl groups, improved the fixation of dyes into PP fiber by increasing the intermolecular forces between dye and fiber.
Oppermann et al. [11] reported the synthesis of disperse dyes with alkyl substituents of varying lengths and dyed unmodified PP with them at a high temperature (125°C) for 150 min. Wash fastness of the dyed samples increased on increasing the chain length of the alkyl substituent; however, the levelness also decreased. An octyl substituent proved an optimum length for good fastness and levelness properties.
Stright et al. [12] reviewed different ways to dye PP including the development of new dyes which were fixed in the fiber by formation of dye-metal complexes on the metal-containing PP fiber, resulting in adequate dyeings in a variety of shades. Dye-metal complex forming dyes could be applied to a wide variety of materials utilizing standard dyeing techniques.
Reactive modification involves treatment of PP fiber with certain chemicals in controlled-conditions [9]. This type of modification increases costs in excess drying, handling, recovery

of materials and operational steps. The treated fibers also showed ring dyeing and inferior physical properties. Reactive modification is thus not a commercially viable option.

Incorporating dye receptive groups in a polymer chain is known as copolymerization, whereas attaching a segment of a dye receptive group as a side chain is termed graft copolymerization [9]. Several disadvantages are associated with the copolymerization of PP:

a. Copolymerization of PP with polar compounds gives low efficiency.
b. Polar compounds impede the crystallization behavior of PP and also decrease the melting point of the polymer.
c. Copolymerization adversely affects the physical and mechanical properties of the polymer.

Graft copolymerization was more technically appealing in the case of PP, but the expensive technology was considered as a barrier to the commercial adaptation [9].

2.1.1 Addition of dye receptors

Addition of dye receptor additives prior to fiber extrusion has been explored by many researchers [9]. Three different classes of these additives are:

a. Metallic compounds
b. Polymeric additives
c. Low molecular weight organic and inorganic compounds

The additive approach can be divided into four major areas of research involving the development of:

a. Disperse dyeable fiber using major disperse, vat and azoic dyes
b. Disperse dyeable fiber using mordant disperse dyes
c. Acid dyeable fiber using anionic dyes used for wool
d. Basic dyeable fiber using cationic dyes

Brown et al. [13] reported disperse and acid dyeable olefin fibers. The dyeable olefin fiber was prepared in two ways: (a) formed a blend of alpha-monoolefin polymer and 1-5% by weight of a pyridine type polymer dye receptor which led to disperse dyeable PP fiber; (b) formed a blend of less than 97% by weight of alpha-monoolefin polymer, 0.5-5% by weight of pyridine type polymer dye receptor and 0.5-5% of hydrophilic compound containing ethylene oxide units. The resultant fibers were dyeable by both anionic and disperse dyes. The approach was to dye the uniformly-dispersed additives so that the whole fiber appeared colored. This approach was found much easier and efficient than fiber pretreatments, copolymerization or grafting, and also less harmful to the fiber's physical properties.

2.1.2 Disperse dyeable PP fibers

The advantages of disperse dyeable PP fibers were:

a. The availability of a wide range of disperse dyes, eliminating the requirement of developing new dyes.
b. The leveling properties of disperse dyes were excellent.
c. Vat and azoic dyes could also be used after a slight modification in the process.
d. The result was excellent wash fastness due to water insolubility.

Grafting of dye enhancers to the polyolefin polymer has been reported by Negola et al. [9, 10]. A mixture of amorphous PETG (glycol-modified polyethylene terephthalate) was grafted onto polyolefin. Maleic anhydride was added to increase the cohesion and dispersion of amorphous PETG in polyolefin polymer. A formulation of 50% PP, 48%

amorphous PETG and 2% maleic anhydride was used and the resultant pellets were extruded into fiber form. A 5% disperse dyeable mixture grafted onto 95% PP resulted, which upon dyeing yielded deep shades, whereas a 2.5% disperse dyeable mixture onto 97.5% PP yielded light shades.

Addition of polymeric dye receptors has been investigated by Farber et al. [14] and Dayioglu et al. [15]. Disperse dyeable PP fiber was manufactured to be consumed in the carpet industry. The approach involved addition of selected polymeric compounds into the PP melt prior to extrusion. Certain limitations of using polar polymeric compounds exist:

a. Subsequent spinning and drawing operations become difficult because most of the polar polymeric compounds lack compatibility with PP.

b. As the polarity of admixing compounds increases, their compatibility with PP decreases. Therefore, polyamides and polyesters with strong polar groups are less compatible with PP than polystyrene and ethylene copolymers.

c. The melting point of most polar compounds is higher which requires a high processing temperature, resulting in the degradation of PP.

d. Many polymeric additives suitable for processing purposes do not have enough polarity to give adequate wet- and dry-cleaning fastness.

e. Most of the polymeric additives require amounts over 10% to be incorporated into the PP fiber to achieve satisfactory dyeability. Large quantities of incompatible and partially-miscible additives adversely affect the physical and mechanical properties of the resulting fiber.

f. The fiber is more costly than the generic version.

In relation to the above challenges, the selection of an appropriate PP additive with all-round adequate properties becomes difficult. An ideal polymeric additive for PP should possess polar groups lying pendant to its chain, be slightly crystalline in nature, have partial compatibility with PP, have a melting point greater that 140oC and have a glass transition greater than 90oC. Polymers such as saturated linear copolyesters, copolyamides, copolymers of vinyl pyridines with styrene, copolymers of ethylene with vinyl acetate and alkyl acrylate may work as such ideal additives.

In conclusion, disperse dyeable PP fibers are comparatively easy to produce and result in level dyeings, although they are more expensive than the generic fiber (usually >$1.00/lb. premium). However, the fastness properties of the dyed materials do not meet all the requirements of the textile and apparel businesses, especially due to their poor dry-cleaning fastness to perchloroethlene (PERC). In addition, a similar chlorinated solvent (trichloroethylene) is commonly used as a spot cleaning agent in carpets, both in manufacturing and in residential/commercial use. The shades obtained by acid and basic dyes are also brighter than those obtained with disperse dyes.

FiberVisions recently launched CoolVisions® (a disperse dyeable PP fiber) [16] having a dye receptor as an encapsulated additive in the polymer matrix. The dye receptor additive is an amorphous, low molecular weight copolyester. A compatibilizer is finely distributed and encapsulated in the microstructure of PP [17]. The modified PP fibers are manufactures by sheath-core bicomponent spinning consisting core as dye receptor and sheath material as PP.

2.1.3 Acid dyeable PP fibers

The advantages of acid dyeable PP fibers include [9]:

a. Acid dyes are inexpensive, offering a wide range of shades with bright colors.

b. Light fastness is excellent.

While most of the acid dyeable PP fiber versions have failed in the development stage itself due to their lack of commercial viability, some of them have shown limited commercial success. Those which have shown commercial success include acid-dyeable PP fiber from Montecatini (Mercalon D®), Hercules (Herculon® Acid Dyeable), Beaunit, Phillips and Toyobo. Out of these, Mercalon D® was dyeable with almost all anionic dyes up to dark shades. Mercalon D® is presently available as a staple fiber for carpets and knitting yarns. Merkalon D®'s use is increasing because its dyeing profile is similar to that of wool. Merkalon D® has a leveling problem in piece dyeing because of its high affinity to acid dyes and high rate of dyeing. Apart from a few limitations and high cost per pound, Merkalon D® fiber appears to have achieved the status of a commercial, general purpose fiber in the carpet and knitting industries.

Arkman et al. [18] reported the mixing of an additive in the PP polymer prior to fiber extrusion. The additive was synthesized by attaching long alkyl chains having substituents such as alkaline nitrogen to a rigid polymer backbone. They found a diffusion coefficient of dyeing in the order of 10-11 m^2/s, which indicated very fast diffusion of the acid dye molecules into the modified fiber driven mainly by the electrostatic interaction between the anionic acid dye and basic dye sites in the polymer contributed by the additive.

The use of Koprolene colors (dyes having a metal chelating group) for modified PP fibers containing nickel salt stabilizer has been reported by Baumann et al., [19] and has demonstrated attractive shades with excellent fastness properties to washing, dry-cleaning, crocking, light and gas fading. The scoured yarn or fabric was recommended to be dyed at 190 to 200°F for one hour and finally to be washed.

2.2 Dyeing mechanism of PP fibers

Since none of the commercially-dyeable PP fiber was available long enough to explore its dyeing behavior [9], only a few scattered studies were reported. The dyeing of hydrophobic fibers with disperse dyes takes place through the solid solution mechanism, i.e., the dye forms a solution within the amorphous region of the polymer. The dye mass transfer from dyebath to the fiber phase is governed by the partition coefficient of the dye. Bird and Patel [20] have shown that the introduction of additional dye into the dye bath beyond the saturation point of the fiber phase did not increase the amount of dye inside the fiber.

Since generic, isotactic PP fiber has only ~30% amorphous mass accessible to dye molecules, the saturation value is low. The encapsulation of a suitable dye receptor additive into the PP matrix causes the amorphous regions of the fiber to increase, leading to the availability of more solvent for the dye to form a solid solution, and thus increasing the saturation values of the fiber. However, the physical properties of the PP fiber, e.g., the percent crystallinity, are lowered when additives are occluded in the solid state structure, and since the cost of the fiber is also increased, both factors detract from use of the modified fiber in textile/carpet products.

2.3 Dyeing of unmodified PP

Calogero et al. [21] reported dyeing of unmodified PP fibers using a colloidal emulsion of water plus long-chain, alkyl-substituted anthraquinone dyes dissolved in an organic solvent. Alkyl chains with carbon numbers from 8-18 were described, and the 18 chain length was found as ideal for PP. The ideal dyebath temperature was reported as 90°C. The dyeing resulted in uniform coloration of the PP fibers with excellent fastness to washing, crocking and dry-cleaning.

Vat dyes captured a large part of the dyestuff market in the coloration of cellulosic fibers because they provide excellent all-round fastness, particularly to light, washing and chlorine bleach. Because of their insoluble nature in the oxidized form, vat dyes require a complicated application procedure involving the reduction of the oxidized form into first the leuco form and then with base into the more water-soluble alkaline leuco form. The soluble, reduced alkaline leuco form has high substantivity towards cellulosic fibers, and after levelness is achieved, the dyes are re-oxidized into the original, water-insoluble keto form inside the fibers.

Sodium dithionite and sodium hydroxide produce large amounts of sodium thiosulfate and sulfites as a byproduct, increasing the cost of effluent treatment. Roessler et al. [22] reported electrochemical methods for reduction of vat dyes which are environmentally friendly, thus providing an alternative to the use of sodium dithionite and sodium hydroxide.

A. V. Mishchenko et al. [23] investigated the batch exhaust dyeing of staple PP fiber at 100°C and 80°C with the acid leuco vat dyes thioindigo red S, thioindigo reddish brown Zh and thioindigo red S (actual chemical structures were not revealed). They plotted a dye exhaustion curve (dye adsorption versus dyeing time) and calculated the heat of dyeing and entropy of dyeing. The heat of dyeing was observed as negative, indicating the strong interaction between the acid leuco vat dye and the PP fiber. The measured heat of dyeing of acid leuco vat dye on unmodified PP was of the same order as that in the disperse dyeing of PP fiber.

The authors also investigated the effect of heat treatment [24] on the fixation of acid leuco dyes on PP fiber. The process sequence involved padding of PP fiber with the acid leuco vat dye solution, squeezing, drying and then treating with dry heat for 1 to 10 minutes. The authors noted that the heat treated fibers resulted in better fastness properties, and thus demonstrated that the heat treatment helped in the fixation of dye molecules via diffusion. The rate of dyeing increased on subsequent heat treatment.

Morozova et al. [25, 26] investigated the process of developing the leuco esters of vat dyes on PP fiber by a nitrite method and optimized the development conditions for maximum color yield:

Temperature: 60°C; development time: 40 min.; liquor ratio: 50; liquor composition: 12.5% H_2SO_4, 2.2 g/l $NaNO_2$. The authors obtained satisfactory light and weathering fastness for the PP dyed with leuco-ester of Vat Brilliant Green S [26].

Bird and Patel [20] studied the dyeing of unmodified PP yarn and film with disperse dyes and concluded that no fundamental difference existed between PP and other substrates in the diffusion mechanism. They showed the Nernst isotherm partition mechanism of dye adsorption between fiber and aqueous phase, which was similar to that followed in the disperse dyeing of polyester fiber. Unmodified PP is more crystalline, nonpolar and hydrophobic than other synthetic fibers [20]. Moreover, the absence of hydrogen bonding groups in PP also precludes the fiber from attaching to the diffused dye molecules, resulting in the poor saturation values. Further, diffusion coefficients of disperse dyes in PP were higher than in cellulose acetate fibers, indicating that diffusion of the dyes inside the PP fiber was not the reason of poor saturation. Weak intermolecular interactions between disperse dyes and PP were concluded to be the reason for the poor saturation values.

According to Ulrich et al. [27], vat dyes when applied in their oxidized or vat acid forms in a colloidal state of dispersion under proper temperature conditions diffuse into highly hydrophobic fibers. Three methods of vat dye application on unmodified polypropylene

fibers were employed: Exhaustion, pad-steaming and printing with steam fixation. Burkinshaw et al. [28] investigated dyeing of textile fibers including: segmented polyurethanes, segmented polyurethane ureas and segmented polyetheresters; polyesters including poly(tetramethylene terepthalate); polyamides including poly(hexamethylene adipamide); and polycaprolactam with acid leuco vat dyes utilizing alpha-hydroxyalkylsufinic acids, their salts and 1, 2, 4-trithiolane as additional reducing agents. The authors reported excellent depth of shade and wash fastness for the dyed materials.

Etters et al. [29] reported that several vat dyes in their acid leuco form exhibited substantivity to unmodified, knitted PP fabrics with C. I. Vat Blue 1, Vat Orange 1 and Vat Yellow 2. Gaehr et al. [30] reported that several Colloisol® vat dyes of BASF exhibited good affinity on plasma-pretreated PP fiber in a pigment pad-thermofix process at 120°C. The fixation of pigments was performed in a pad-steam or pad-dry heat process, and the processes were reported to be applicable for dyeing of fiber mixtures containing PP.

3. Literature review summary and scope of the research

From the literature review, the substantial volume of work conducted by researchers of different laboratories world-wide confirmed that the aqueous dyeing of generic, unmodified PP fiber is of significant importance for textile, carpet, apparel, sportswear and a variety of other product applications. Most of the work carried out by researchers included the modification of PP fiber in some form or another, paths which although they impart dyeability, increase the total fiber costs two to three times above that of generic PP because of utilization of a variety of modifying chemicals, additives, comonomers or components. Another disadvantage of the fiber modification route is that it adversely affects the mechanical and physical properties of the fiber. The low cost and good physical/aesthetic properties, the two basic motivations for utilizing generic PP fiber in textiles and carpets, have been outweighed by the disadvantages and limitations of modifying the fiber solely to impart aqueous dyeability.

The primary purpose of the aqueous dyeing of PP fiber in its generic, unmodified form is to exploit the advantages this fiber offers to the market place and, at the same time, create new product markets for this inexpensive fiber in high volume consumption areas such as tufted carpets, towels, apparel, sportswear and technical textiles. These product markets are governed today by demand-activated manufacturing, and hence can only be realized by developing flexible, aqueous batch and continuous dyeing processes for generic PP consistent with commercially-established coloration technologies already in use for other high-volume, commodity fibers.

4. Technical approach

The coloration of cellulosic fibers with vat dyes is well established [31]. However, hydrophobic fibers such as PP are not dyeable by the conventional, aqueous-based methods which are successful for cellulosic fibers in which the alkaline leuco, dianion form (completely water soluble) of vat dyes is utilized. Theoretically, acid leuco vat dyeing analogous to the disperse dyeing of polyester fiber may provide a method to aqueous color unmodified PP fiber. Etters et al. [29] among others [23, 24, 27] reported the acid leuco vat dye route as a potential path to aqueous dyed PP fiber in its unmodified form.

Recently, researchers [32, 33] investigated the process of dyeing polyester with indigo vat dye utilizing the non-ionic, acid leuco form of indigo (sparingly water soluble) to dye polyester fabrics and obtained good fastness results by optimizing the concentration of sodium hydroxide and sodium hydrosulphite. The authors noted that using excess sodium dithionite eliminated the need to back-titrate with acetic acid to achieve the acid leuco form of the vat dye [32].

The correlation between dye exhaustion and the solubility parameter for PLA fiber and disperse dyes has been reported by Karst et al. [34, 35] , who showed that the closer the solubility parameter of the dye was to the fiber, the better the exhaustion of the dye. Solubility parameter (SP) is the square root of the cohesive energy density. SP of the PP and commercially available vat dyes were calculated using the Fedors group contribution method [36]. Dyes having SP values closest to that of PP were given priority in this research. Calibration curves for each dye were prepared using UV/Vis NIR Spectrophotometry. The single stage, acid leuco vat dyeing process was utilized to dye the PP flat fabric. Various mixing parameters (Flory-Huggins interaction parameter and free energy of mixing) were predicted using Accelrys' Materials Studio® software. Dyes having the least free energy of mixing with PP were given priority in the experiments.

Exhaust batch dyeing experiments were conducted on a single bath Roaches Colortec® High Temperature Dyeing Machine at Georgia Tech, as well as on a Roaches Pyrotec Multi-Beaker Dyeing Machine at the University of Georgia, utilizing the optimized, single stage acid leuco dyeing procedure. Percent exhaustion was measured to evaluate the efficacy of each dye.

Dyed fabrics were evaluated for various fastness properties (washing, crocking and dry-cleaning) in order to certify the viable vat dye candidates. The impact of the dyeing process on the solid state structure of PP was investigated using X-ray diffraction and tensile testing. Rate of dyeing plots were prepared for the single dyeings as well as for combination dyeings. Adsorption isotherms were prepared to calculate the thermodynamic parameters of dyeing for single colorants. The K/S values of the dyed samples were determined.

In order to perform the continuous steam-pad dyeing, the PP fabric was dipped and squeezed into the solutions 2-3 times to perform the padding operations using dye pad and chempad formulations. The developed, optimized pad-steam process sequence for simulated continuous pad/steam coloration of unmodified PP fabric with acid leuco vat dyes was based upon the method first described by Ulrich et al. [27]. The fabric was padded into the dye pad formulation, dried in a convection oven, padded with the chempad formulation, steam-fixed in the lab box steamer and finally cold-rinsed, soaped, washed and air-dried.

The simulated continuous pad-dry heat process was based on the diffusion of acid leuco vat dye molecules into the swollen amorphous regions of the PP fiber at a temperature of 130°C. The PP fabric was padded into the vat acid formulation, the excess squeezed out by hand, and the saturated fabric placed into a forced convection oven at 130°C for 10 minutes.

5. Results and discussion

5.1 Solubility parameter calculations

The chemical structures of oxidized vat dyes were obtained from the Colour Index, 1971 Edition [37]. The chemical structures of the corresponding reduced acid leuco vat dyes were

determined using the general hydrosulfite/hydroxide reaction. The Fedors group contribution method was applied after structural analysis of the acid leuco vat dyes to compute the solubility parameter. The table of atomic and group contributions to energy of vaporization and molar volumes from Fedors was used in this computation [36].

Table 5.1 shows the calculated solubility parameters (SPs) for oxidized and reduced vat dyes in which Vat Red 15, Vat Orange 7, Vat Yellow 2, Vat Blue 18 and Vat Orange 1 have the lowest values. The solubility parameter of PP was calculated to be 8.1 $(cal/cm^3)^{1/2}$. Since Vat Red 15 and Vat Orange 7 are cis- and trans- isomers, respectively, the two molecules yielded equal solubility parameters.

C.I. Name of Dye	C. I. Constitution Number	Calculated SPs $(cal/cm^3)^{1/2}$ for Keto Form	Calculated SPs $(cal/cm^3)^{1/2}$ for Acid Leuco Form
Vat Red 1	73360	13.9	16.0
Vat Yellow 2	67300	13.7	15.0
Vat Blue 6	69825	15.3	18.6
Vat Orange 1	59105	13.0	14.6
Vat Blue 1 (Indigo)	73000	13.9	16.7
Vat Brown 1	70800	15.5	19.3
Vat Red 15	71100	14.2	14.4
Vat Yellow 33	65429	14.3	16.0
Vat Red 13	70320	13.4	14.8
Vat Orange 7	71105	14.2	14.4
Vat Yellow 4	59100	13.6	15.6
Vat Violet 1	60010	12.1	14.8
Vat Violet 13	68700	14.9	16.6
Vat Black 27	69005	15.1	17.5
Vat Green 8	71050	15.3	19.1
Vat Orange 2	59705	13.4	14.8
Vat Blue 18	59815	13.1	14.5
Vat Green 1	59825	13.5	14.9
Vat Red 10	67000	15.1	18.4
Vat Orange 15	69025	14.6	16.7

Table 5.1. Calculated Solubility Parameters of Vat Dyes Using Fedors' Method [36]

5.2 Chemistry of acid leuco dyeing

The four stages of reduction of C. I. Vat Orange 1 dye (Fig. 5.1) indicate that excess sodium hydrosulphite acts as an acid in addition to being a reducing agent for the carbonyl groups, and the chemical thus converts the alkaline leuco form of vat dye (II) into first the monoioninc leuco form (III) and, with further addition of sodium hydrosulphite, into the nonionic (acid leuco) form (IV):
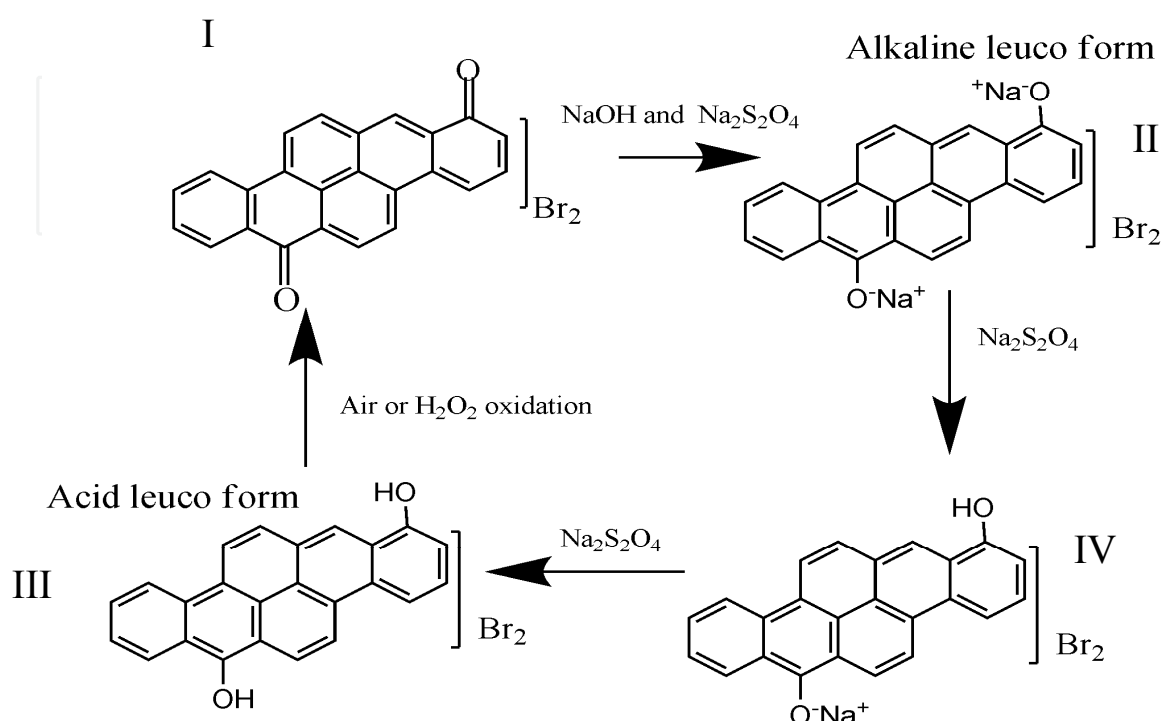
Vat orange 1

Fig. 5.1. Various Stages of Conversion of Vat Orange 1 from the Keto to the Acid Leuco Structure: (I) Original Keto Structure; (II) Alkaline Leuco; (III) Monoionic; and (IV) Acid Leuco

The neutral acid leuco form has been reported as having affinity with hydrophobic fibers such as polyester and PP [27, 32, 33].

5.3 Chemical structures of vat dye candidates for the PP single-stage, acid leuco vat dyeing process

Figure 5.2 shows the conversion of a vat dye into its acid leuco form with the action of sodium hydroxide and excess sodium hydrosulphite. The acid leuco forms were utilized to calculate the solubility parameters of the vat dyes using Fedors' group contribution method (Table 5.1).

From the Colour Index search, the chemical structure of C. I. Vat Blue 8 deemed it a candidate for the dye trichromatic series (Figure 5.2 e). The SP for Vat Blue 8 was calculated in its acid leuco form to be 15.4 $(cal/cc)^{1/2}$, which was lower than those of Vat Blue 6 (18.6 $(cal/cc)^{1/2}$) and Vat Blue 1 (16.7 $(cal/cc)^{1/2}$). The predicted mixing energy was also much lower for Vat Blue 8 (10.2 kcal/mole) than Vat Blue 6 (22.1 kcal/mole), further strengthening the theory that Vat Blue 8 could be a more viable performer than Vat Blue 6 in the trichromatic series. However, an exhaustive search of dye vendor sources revealed that Vat Blue 8 is currently not commercially available on the world

market, thus precluding its experimental confirmation as a viable vat blue colorant for generic PP.
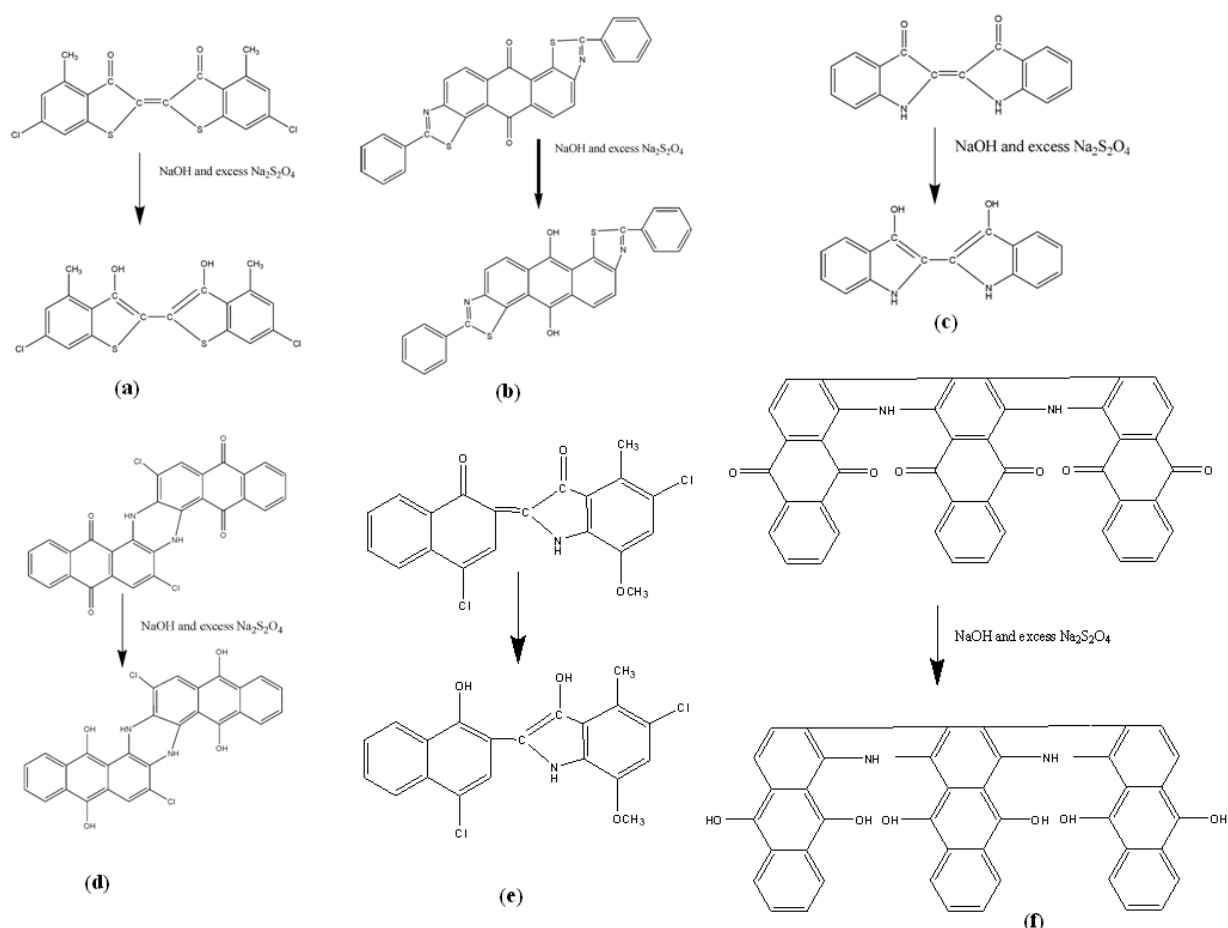

Fig. 5.2. Conversion of Oxidized Vat Dye Keto Structures into Reduced Acid Leuco Structures: (a) Vat Red 1; (b) Vat Yellow 2; (c) Vat Blue 1 (Indigo); (d) Vat Blue 6; (e) Vat Blue 8; and (f) Vat Brown 1

5.4 Predicted free energy of mixing of acid leuco vat dyes at 90°C using accelrys' materials studio$^{®}$ software

Mixing energies of different acid leuco vat dyes with isotactic PP chain of DP=10 were predicted using Accelrys' Materials Studio® (MS) software. The Blends Analysis Feature of the MS software was used to perform dye-PP mixing simulations. The results in Figure 5.3 demonstrated that the dyes C. I. Vat Blue 1, Vat Blue 8, Vat Red 1, and Vat Blue 6 had the lowest free energy / interaction parameters of mixing with PP. Vat Orange 1 and Vat Yellow 2 were intermediate in the parameters, while Vat Brown 1 had the highest free energy / interaction parameter of mixing. Vat Brown 1 was thus predicted to have poorer interactions with isotactic PP and resulting poorer exhaustion and color strength (K/S value) properties than the other dye candidates, predictions that were later confirmed by the exhaust batch dyeing experimental data.
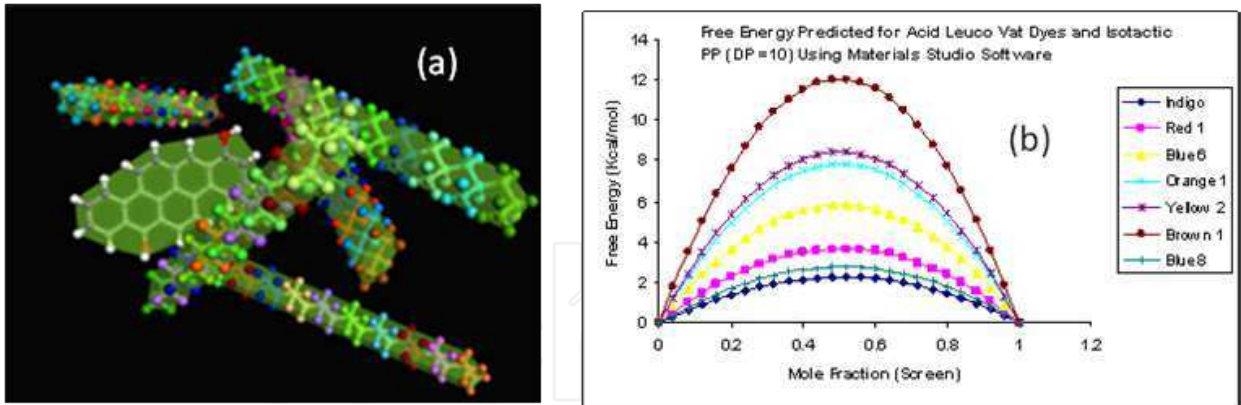
Fig. 5.3. (a) 3-D space Configuration of Vat Orange 1 Interacting with Isotactic PP in Materials Studio Workspace; (b) Free Energy vs. Mole Fraction of Different Dyes with PP at 363°K Predicted Using Materials Studio® Software

5.5 K/S value determinations

The Ultrascan XE sensor was standardized using a light trap and the standard white tile. The sensor was tested for accuracy before PP fabric measurements by scanning the diagnostic green tile, and then comparing the X, Y, Z tristimulus values obtained with the values printed on the green tile. Ten readings taken at different places were recorded for each of the dyed fabric samples, and the average of the ten readings was computed to derive the K/S value for each sample at the wavelength of minimum fabric reflectance. The K/S results in Table 5.2 revealed a correlation with the blend miscibility approach for the candidate six vat dyes, e.g., C. I. Vat Brown 1 gave the least color transfer onto the PP fabric due to its very high solubility parameter/mixing energy.

C.I. Name of Dye	Wavelength of Minimum Reflectance (nm)	K/S at Wavelength of Minimum Reflectance	SP (Acid Leuco Form) $(cal/cm^3)^{1/2}$
Vat Red 1	510	4.4	16.0
Vat Blue 6	600	3.9	18.6
Vat Yellow 2	420	2.1	15.0
Vat Orange 1	440	5.0	14.6
Vat Blue 1	640	6.1	16.7
Vat Brown 1	400	1.7	19.3

Table 5.2. Final K/S Values of PP Fabrics Colored by Single Stage Vat Acid Leuco Dyeing Method (8% owf)

The K/S versus % owf plot detailed that for all dyes, increasing the amount of colorant in the dyebath resulted in a gradual color buildup on the dyed fabric, followed by saturation (Figure 5.4). K/S values of the colored fabrics with the colorants of the trichromatic series plus orange exhibited similar K/S plots, whereas those dyed with Vat Blue 1 exhibited much higher K/S values, reinforcing the compatibility of the component colorants of the trichromatic series plus orange colorants in PP fabric dyeing, along with the incompatibility of Vat Blue 1 with the group.
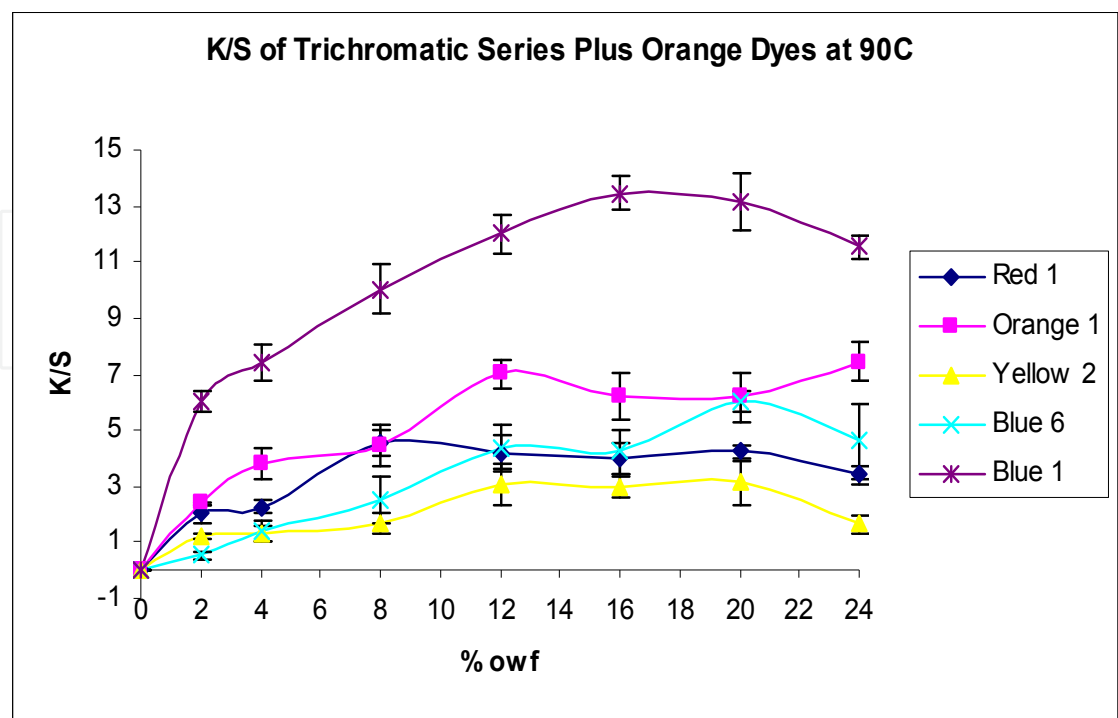
K/S of Trichromatic Series Plus Orange Dyes at 90C

Fig. 5.4. K/S Values at Wavelengths of Minimum Reflectance versus % owf for Acid Leuco Vat Dyed PP Fabrics

5.6 Correlation of experimental K/S values with calculated acid leuco dye solubility parameters and predicted mixing energies

Figure 5.5 showed the correlation between K/S values of dyed PP fabrics and calculated SP/predicted mixing energies of six acid leuco vat dyes. Upon increasing solubility parameter and mixing energy from Vat Blue 1 to Vat Brown 1, the K/S value decreased. This correlation demonstrated the viability of the theoretical approaches (calculated SP and predicted mixing energy) to screening viable vat dye candidates for the coloration of generic PP.

The predicted mixing energy for Vat Orange 1 was high, but the corresponding high experimental fabric K/S value and low acid leuco vat dye SP value created an anomaly (Figure 5.5). The discrepancy was explained by the more complicated, high molecular weight chemical structure of C. I. Vat Orange 1 compared to the other certified dyes (MW = 468 g/mole, six fused aromatic rings in a benzenoid structure with a plane of symmetry running through the molecule, a dibromine salt, etc., Figure 5.1). Figure 5.3(a) models the difficulty in placing the Vat Orange 1 molecule within the polymeric chains of PP in the amorphous regions. In addition, utilizing the "like dissolves like" rule of organic chemistry and designating PP as the solvent and the Vat Orange 1 as the solute, the highly aromatic nature of the dye dictates poor compatibility with the aliphatic PP chains. Utilizing these two factors, the Materials Studio® Software predicted a comparatively high mixing energy between PP and Vat Orange 1 (Figure 5.3(b)). With the experimentally-observed high K/S value for the dyed fabric, however, the low SP of Vat Orange 1 (14.6 (cal/cc) $^{1/2}$) was a more accurate predictor of the good compatibility of the colorant with PP than was the mixing energy (Figure 5.5).
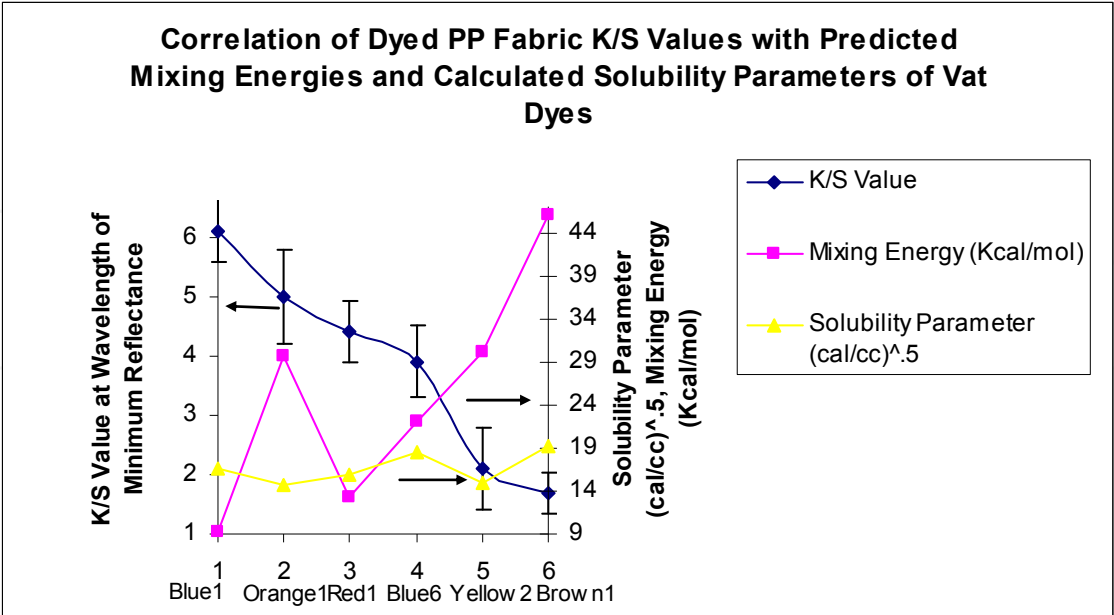
Fig. 5.5. Correlation of Dyed PP Fabric K/S Values with Calculated Acid Leuco Dye Solubility Parameters and Predicted Mixing Energies

5.7 Evaluation of fastness properties
5.7.1 Fastness to crocking
Crock fastness was determined using the electronic crock meter with 10 complete cycles in both dry as well as wet conditions according to AATCC Standard Test Method 8-2004. Vat Blue 6 exhibited less resistance to crocking as it stained the cotton cloth square to a rating of 3-4, whereas Vat Orange 1, Vat Red 1, Vat Blue 1 and Vat Yellow 2 all showed good to excellent crocking resistance (Table 5.3). The higher crock fastness ratings in the wet condition to that of the dry condition was attributed to the reduction in the frictional force between the low surface energy PP fabric and the rubbing finger of the crock meter caused by the lubricating effect of water at the interface.

C.I. Name of Dye	Staining Rating	
	Dry	Wet
Vat Orange 1	4	4-5
Vat Yellow 2	4-5	4-5
Vat Blue 6	3-4	4
Vat Red 1	4	4-5
Vat Blue 1	4	4

Table 5.3. Crock Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

5.7.2 Fastness to washing
Wash fastness of the dyed materials was determined by AATCC Standard Test Method 61-2003, no. 2A. The fastness ratings (Table 5.4) revealed that Vat Orange 1 exhibited excellent wash fastness on the PP fabric, whereas the other vat dyes yielded good, acceptable wash fastness properties to the PP fabric.

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Orange 1	5	5	5	5	5	5	5
Vat Yellow 2	5	4-5	4-5	5	4-5	5	4-5
Vat Blue 6	5	4-5	4-5	4-5	4-5	4-5	4-5
Vat Red 1	5	4-5	4-5	4	4-5	4-5	4-5
Vat Blue 1	5	4-5	5	4	4-5	5	4-5

Table 5.4. Wash Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

5.7.3 Fastness to dry-cleaning (Perchloroethylene)

Dry-cleaning fastness of the dyed materials was determined by AATCC Test Method 132-2004. The fastness ratings confirmed that all of the certified vat dyes imparted good, acceptable dry-cleaning fastness properties to dyed PP fabric (Table 5.5).

C.I. Name of Dye	Change in Color	Staining on the Various Components of Multifiber Fabric Style # 10					
		Acetate	Cotton	Nylon 66	Polyester	Acrylic	Wool
Vat Orange 1	5	5	4-5	4-5	4-5	4-5	4-5
Vat Yellow 2	5	4-5	4-5	4-5	4	4-5	4-5
Vat Blue 6	5	4-5	4	4	4	4	4-5
Vat Red 1	4-5	5	4	4-5	4-5	4-5	4-5
Vat Blue 1	4-5	4-5	4	4-5	4-5	4-5	4

Table 5.5. Dry-Cleaning Fastness Ratings of PP Fabrics Dyed with Certified Vat Dyes

C.I. Name of Dye Change in Color Staining on the Various Components of Multifiber Fabric Style # 10

6. Conclusions

Solubility parameter and molecular dynamics simulation approaches were developed to screen viable vat dye candidates for generic PP aqueous dyeing, and the dyes targeted as viable candidates by the theoretical techniques provided excellent experimental correlations, e.g., high color yields, in dyeing PP fabrics by the optimized acid leuco vat process.

A viable method to commercially aqueous batch dye generic, unmodified PP fiber textiles in a conventional process has been developed for a certified trichromatic series (red, yellow and blue) plus orange of vat dyes with adequate fastness properties to washing, crocking and dry-cleaning in their acid leuco forms: C. I. Vats Red 1, Yellow 2 and Blue 6 plus Orange 1. The same method was shown to adequately color PP textiles with C. I. Vat Blue 1 (Indigo) as a stand-alone colorant with adequate fastness properties to washing, crocking and dry-cleaning to produce the popular "denim" shade. The developed single-stage acid leuco method for dyeing generic PP fabrics at pH 7 provided good fastness properties and good color yields without fiber "ring-dyeing."

Of the vat dyes currently available on the commercial market, C. I. Vat Dyes Orange 1, Yellow 2, Red 1 and Blue 1, all possessing low solubility parameters closest to that of generic PP's 8.1 (cal/cc)$^{1/2}$, were demonstrated to be viable candidates for generic PP fiber coloration, while C. I. Vat Blue 6 was deemed a marginal candidate. However, Vat Blue 6 was the best-performing blue vat dye available outside of Vat Blue 1, and since the latter

was so easily air-oxidized compared to the other candidates for the trichromatic series and was thus incompatible with them, Vat Blue 6 was judged sufficient in performance to move the technology forward into practice.

An exhaustive survey of blue vat dye structures in the Colour Index yielded one colorant that possessed the proper solubility parameter and heat of mixing with PP characteristics: C. I. Vat Blue 8. However, the colorant is no longer commercially available on the world market, but with the viable aqueous PP coloration process now developed, vat dye manufacturers will have incentives to bring Vat Blue 8 back into production.

7. Acknowledgment

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