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Polymeric colorants*

J. Miley

The Roger Milliken Center, 920 Milliken Road, Spartanburg, SC 29304, USA

Abstract - The search for more readily available sources of coloration over the last century led to the development of synthetic pigments and dyes. This search in turn fathered modern industrial chemistry. Today a new class of materials, polymeric colorants, has gained recognition and applicability as an alternative to these classical methods of coloration. The marriage of polymer and dye chemistries enables the chemist to design unique materials that exploit the best characteristics of both pigments and dyes. The motivation for the development of this exciting new class of materials is performance. This paper will explore some specific examples of polymeric colorants that have appeared during the last two decades and show how they uniquely meet functional requirements.

INTRODUCTION

A polyurethane foam puzzle, a reaction injection molded steering wheel, bonded carpet pad, a bowling ball, wood flooring, soluble plant food, a household fabric softener, a newspaper insert, all colored in whole or in part with polymeric colorants -- but why ? If the answer were, "because it can be done", then these applications would be commercial failures; their success is testimony to the fact that it is possible to build function into polymeric colorants that cannot be matched by either pigments or classical dyes.

But pigments and classical dyes have and will continue to serve many markets well. In fact, both organic color pigments and synthetic dyes have reached or are approaching 1 billion dollars in sales in the US alone as shown in Table 1. Every segment of these attractive markets is a potential target for the polymeric colorist with the caveat that he must deliver exceptional value to penetrate an established dye or pigment application. One can usually identify compromises and shortcomings made in a given application to accommodate conventional dyes or pigments; however, to replace them with new technology, one is faced with the trade-offs of potential market sales, development cost, complexity of offering, and time to enter the market. The more narrow the application, the greater the opportunity to build in unique features, the longer the time to break-even on R&D cost and the greater the complexity of manufacturing.

By examining current applications for polymeric colorants at Milliken and in recent literature we can extract some lessons about the design of polymeric colorants and the types of benefits they can provide.

TABLE 1 MAJOR U.S. MARKETS FOR ORGANIC PIGMENTS AND DYES[1]

MARKET	SIZE			
	ORGANIC COLOR PIGMENTS 1992		SYNTHETIC DYESTUFFS 1994	
	M TONS	MM $	M TONS	MM $
PRINTING	33.7	510	8.6	100-110
COATINGS	9	250	-	-
PLASTICS	7.1	175	4	50-60
PAPER	1.2	18	. 39.9	180-200
TEXTILES	1.3	21	85.6	750-850
DETERGENTS	-	-	31.8	120-140
MISC.	0.3	21	9.2	90-100
TOTAL	52.6	995	179.1	1,215

**Dedicated to Dr. Hans H. Kuhn in his 35th year at Milliken & Company*

WHY POLYMERIC COLORANTS ?

The motivation for designing polymeric colorants is to overcome the deficiencies of both dyes and pigments in particular applications. One can think of a dye as a virtually isolated chromogen and a pigment as an agglomeration of chromogens.

When the dye is dissolved in a solvent, every chromogen is available to absorb light, and the solution is clear. Other advantages of dyes are their solubility and non-abrasiveness. However migration, sublimation, solid nature, price, and the toxicity of dyes can be a concern. By contrast, the same concentration of a pigment dispersion absorbs less light than that of the dye since many of the pigment chromophores are "in the shadow" of other chromophores. This dispersion is not perfectly clear because light scatters and reflects to an extent determined by the particle size of the pigment and its refractive index relative to the vehicle. Pigments usually do not have the same migration, toxicity, and sublimation problems of dyes; however, the disadvantages of pigments are their insolubility, solid nature, abrasiveness, and their reduced efficiency of absorbing light.

An alternative to the aforementioned possibilities is a polymer-bound chromogen(s). Figure 2 suggests a number of possible structures.

Figure 1

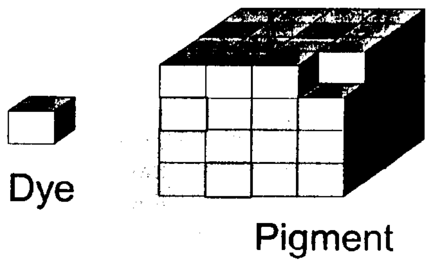


Figure 2 Polymeric Colorants

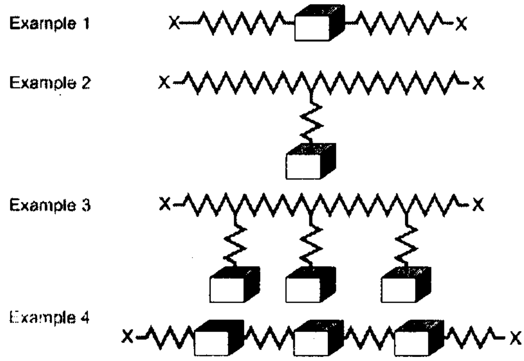
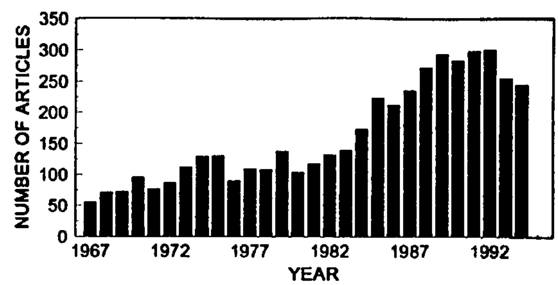


Table 2: Comparison of the Properties of Pigments, Dyes and Polymeric Colorants

PROPERTY	PIGMENT	DYE	POLYMERIC COLORANT
Solubility	Insoluble	Soluble	As Designed
Lightfastness	High	Moderate	As Designed
Migration	No	Yes	As Designed
Sublimation	No	Yes	No
Abrasive	Yes	No	No
Absorption	No	Yes/No	As Designed
Price	Low	High	Often Higher
Viscosity	Solid	Solid	As Designed
Toxicity	Low	A Concern	Low

Figure 3: Chemical Abstracts References. Color with polymer vs. year



Polymeric colorants proffer the advantage of allowing a range of physical properties (Table 2). Their solubility, absorption, migration, and viscosity are tunable. They do not sublime, are non-abrasive, and generally have low toxicity. Furthermore, as this paper will demonstrate, these properties can be used to add value to special applications while preserving the perceptual attributes of the color inherent to the chromogen.

The range of product possibilities offered by the joining of the fields of polymer chemistry and color chemistry is virtually inexhaustible. New examples frequent many journals of chemical literature (Fig. 3). There are reviews that summarize the area.[2,3] Guthrie covers the literature up to 1990 with an emphasis on "color within the context of practical applications." He accurately describes these materials: "Polymeric colorants are a group of intermediate or high molar mass compounds that ...(are)... intrinsically coloured."

RECENT POLYMERIC COLORANT APPLICATIONS

Some newer applications of polymeric colorant are given in Table 3. Even though the applications are very different there are recurrent themes with regard to properties and benefits.

Table 3: Recent Examples of Polymeric Colorant Applications

APPLICATION	PERFORMANCE BENEFITS	REF.
Non-linear Optics (NLO) Optical Data Storage	Clear films, high chromogen density, non-migration, no crystallization or precipitation, ease of fabrication, controlled solubility	4, 5, 6, 7, 8, 9, 10, 11, 12, 13
Experimental Molecular Probes/ Diagnostic Testing	Controlled absorption, controlled orientation, increased water solubility, higher chromogen density, non-toxic, non-irritant, bioinert	14, 15, 16, 17, 18, 19, 20
Photography	Higher chromogen density, non-migration, higher water solubility	20, 21, 22, 23, 24
Printing	Controlled melting point, non-migration, non-staining, compatibility with plasticizers	25
Bulk Coloration of Polymer	Solubility, low volatility, low toxicity, low irritation, non-extraction, thermal stability, high chromogen density	26, 27
Photoresist	High chromogen density, non-migration, low volatility, no extraction, no crystallization	28

MILLIKEN COLORANTS

Milliken has produced polymeric colorants for nearly 35 years (Table 4). Today many unique polymeric colorant-based product areas exist, each designed to meet the needs of specific markets. For example, Versatint® colorants are used to color code textile fibers during processing yet disappear in the final dying and finishing step, without adding any extra processing steps and without influencing the final shade of the fabric -- even if it happens to be white. In direct contrast, Reactint® colorants are chromogen-bearing polyols that covalently bind to polyurethanes to give permanent color. Any ClearTint® colors are colors designed for polyolefins and other plastics and are neither reactive nor fugitive! Each of these families of polymeric colorants was designed to have unique properties so as to meet identified market needs.

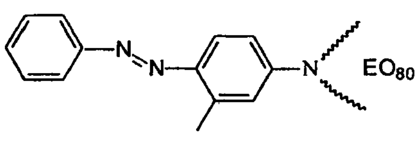
Table 4: Milliken Colorant Products

PRODUCT LINE	TYPICAL APPLICATION
Versatint®/Syltint®	Fugitive tints for textiles
ClearTint®/Advantage®	Clear, bright color concentrates for polyolefins
Reactint®/BondTint®	Reactive polyurethane colorants
Palmer™	Non-staining washable colors for markers
Liquitint®	Consumer products for detergents, softeners, etc.
Blazon®/Bullseye®	Spray pattern indicator for golf courses, agricultural applications

FUGITIVE TINTS

Textile fibers go through many processes, such as spinning, weaving, and dying and finishing, during their conversion to useful fabrics. These operations are sequential and are often at separate locations. Inspection of the final fabric for defects prior to shipment may take days or even weeks. In the initial steps, defects caused by the mixing of yarn types cannot readily be seen until the end of these processes. Color-coding the various types of fibers prevents such errors and the consequent damage. These "fugitive tints" can be totally removed so that they do not influence the final shade of the fabric.

H. Kuhn disclosed the first examples of polyoxyalkylene polymeric colorants that fulfill these performance requirements in 1964.[29,30] These large, highly water-soluble molecules could not penetrate the fiber surface and could readily wash away during normal aqueous dyeing and finishing.

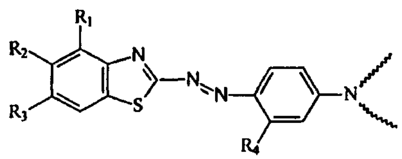


POLYURETHANE COLORANTS

Another example of designing multiple performance features into a product line is shown by Milliken's colorants for polyurethanes.[31] Polyurethanes are produced via the reaction of an isocyanate and a polyol. Reactint® colorants are liquid polyol-bound chromophores compatible with both polyether and polyester flexible foam systems. The colorants do not settle, separate, or interfere with cell structure like some pigment dispersions.[32] Because they are good lubricants as opposed to pigment dispersions, they are benign to pumps and check values.[33] By blending five primary colors almost any desired hue is obtainable.

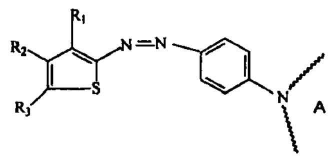
The task of developing these colors turned out to be more formidable than anticipated. Components in a forming foam are simultaneously exposed to high temperatures, excess isocyanates, reducing conditions, strong bases, and, sometimes, alkylating flame retardants. These conditions preclude the use of many functionalities like nitro groups, active hydrogens, and base-sensitive substituents. Table 5 shows how the substituted benzothiazolyl azo system can vary in resistance to reduction while Table 6 shows that thiophene azo colorants can exhibit stability under similar conditions.[34]

Table 5: Effect of Stannous Octoate on Benzothiazolyl Colorants



R_1	R_2	R_3	R_4	% LOSS	COLOR
H	H	OMe	Me	56.5	RED
Cl	H	H	H	91.5	RED
OMe	H	H	OMe	66.7	RED
Me	H	Cl	H	85.9	RED
Cl	H	H	Cl	97.8	RED
Cl	H	Cl	H	87.9	RED
H	Cl	Cl	H	100	RED

Table 6: Effect of Stannous Octoate on Thiophene Azo Colorants



R_1	R_2	R_3	R_4	% LOSS	COLOR
CO_2Et	Me	CO_2Et	Me	5.3	RED
CN	$-(CH_2)_4-$		H	3.2	RED

With the appropriate selection of chromophores and selection of polyol tails, polymeric colorants sufficiently robust for these conditions can be achieved, and furthermore, the perceptual attributes of the foams need not be sacrificed.[35] Figure 5 compares foams colored with polymeric colorants to foams colored with analogous dyes. In each case, virtually the same hue is achieved without sacrificing the chroma (C) or lightness (L).

MARKER INKS

Water-based marker inks made with typical acid dyes, like Acid Red 1, Acid Blue 9, Basic Violet 17, etc. yield bright colors at relatively low cost; however, these acid dyes stain proteinaceous materials like skin, silk and wool, as well as polar fibers like nylon and cotton. It seemed obvious that fugitive tints could be modified to incorporate bright chromogens to produce non-staining colors for marker inks. In fact this was not the case because ink viscosity had to be low, restricting the overall molecular weight. In lower mol.wt. weight materials, the chromogen represents a high percentage of the polymeric colorant and affects staining.

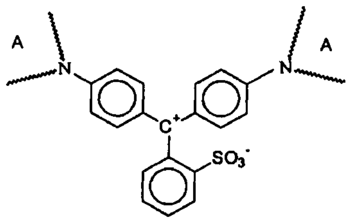
For example, Acid Blue 9 can be modified with varying moles of ethylene oxide as shown in Table 7.[36]

Clearly a trade-off exists between the polymeric colorant's washability from skin and from cotton fabric. Basic Violet 1, did not respond as strongly as Acid Blue 9.

Another class of chromogens that yield attractive shades on paper are the benzothiazole azo colorants. The unsubstituted color is a beautiful red. Optimizing the polymer chain did give low staining of skin; however, it did not sufficiently improve the staining on cotton. Addition of a sulfonic acid group further improved the cotton staining but also shifted the shade bathochromically.

Nevertheless, the appropriate selection of polymer-bound chromophores do deliver the desired physical properties; and again those properties can be achieved while maintaining the perceptual attributes of the inks. Figure 6 compares inks formulated with polymeric colorants and inks formulated with their analogous dyes. Again in each case, the hue, chroma, and value of the colorant samples match well the dye samples.

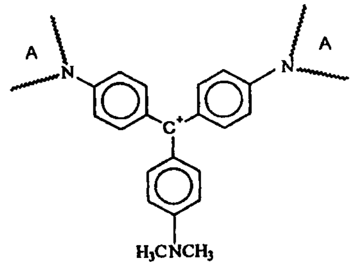
Table 7: Performance of C.I. Acid Blue 1 Derivatives as a Function of Composition



1 A	2 VIS (cps) @ 25°C	3 DELTA E*	4 HAND STAINING
27 EO DA	19.1	17.2	0
10 EO DA	2.5	6.3	2
6 EO DA	3.1	5.3	2
4 EO DA	1.9	6.2	4
70 EO	SOLID	15.9	0
35 EO	58.4	23	1
20 EO	5.3	8.2	0
15 EO	6.3	5.2	1
12 EO	5.3	4.6	1
10 EO	1.7	4.1	2
8 EO	3.1	4.4	1.5
6 EO	3.1	5.3	2
4 EO	2.5	6.3	4

1. EO = Moles ethylene oxide DA = diacetate terminal groups
2. VIS (cps): Brookfield LVT viscosity at equal color strength.
3. Δ E: CIELAB color difference of stained and washed fabric.
4. STAINING: 0 = no stain: 5 = moderate: 10 = severe

Table 8: Triphenylmethane Polymeric Colorants without a Polar Group



1 A	2 VIS(cps) @ 25°C	3 DELTA E*Δ	4 HAND STAINING
4 EO	1.5	31	5
5 EO	1.6	28	7
10 EO	1.9	15	3
20 EO	1.9	22	2
20 EO DA	1.9	20	3
70 EO	2.5	38	1

1. EO = Moles ethylene oxide DA = diacetate
2. V (cps): Brookfield LVT viscosity at equal color strength.
3. Δ E: CIELAB color difference of stained and washed fabric.
4. STAINING: 0 = no stain: 5 = moderate: 10 = severe

Figure 5: Comparison of Dye and Colorant Based Foams

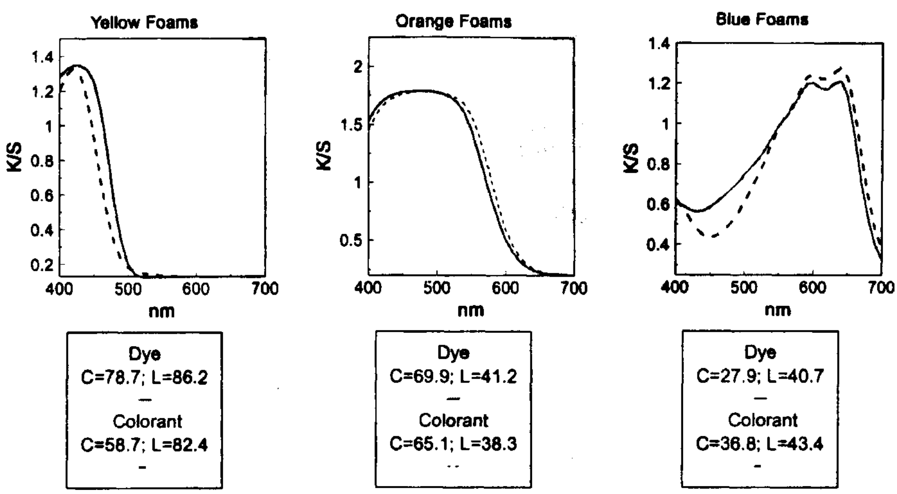
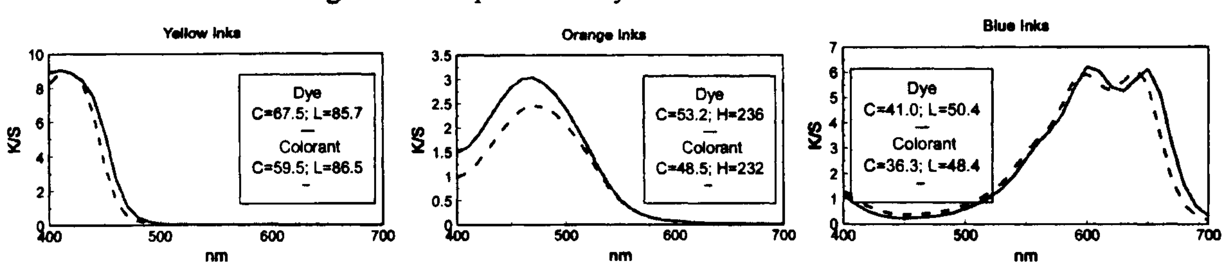


Figure 6: Comparison of Dye and Colorant Based Inks



CONCLUSIONS

1. The highest activity in polymeric colorants in the last 5 years has been in the areas of non-linear optics/optical data storage and diagnostic systems. In these areas and others listed in Table 3, the key performance benefits are increased chromogen density, controlled solubility, controlled migration, controlled absorption, modified physical properties, etc., much the same as was found by Guthrie for prior years. It is difficult to generalize because each application is unique and has its own set of design criteria.
2. Polymeric colorants, the product of combining polymer and color chemistry, offer incredible versatility in addressing application requirements.
3. The polymeric colorist has to become well versed in a given application before it is possible to effectively innovate.
4. Examples have been cited in the recent literature and in our polymeric colorant work at Milliken that illustrate successful examples of providing the types of benefits listed in Table 9.
5. Polymeric colorants can be the most appropriate product embodiment when a combination of the properties of pigments and dyes is needed or when nothing already exists that will meet the performance requirements of a given application.

TABLE 9

PERFORMANCE BENEFITS OF POLYMERIC COLORANTS
High strength colors
Clear colored coatings and films
Non-leaching colors
Non-abrasive liquid colors
Reduced toxicity and irritation
Colors with modified physical properties

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