SUCCESS STORIES IN INK, PAINT AND PLASTICS APPLICATIONS

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INTRODUCTION

To some people the term, Environmentally Acceptable Pigments is an oxymoron. To others it is fantasy; after all, how can one effectively replace products like chrome yellow or cadmium red. These products have been used successfully for decades in inks, coatings or plastics applications. However, a growing number of pigments users are monitoring the performance of these metal containing pigments with ENVIRONMENTALLY ACCEPTABLE PIGMENTS. The following success stories review some of the difficulties that these pigment users had to overcome to be successful.

First replacement of barium-based pigments has become an area of concern, particularly for producers of printing inks used in packaging applications.

Reduction of VOC's is a very important issue to ink and coatings manufacturers. High solids and water-borne systems will continue their rapid growth. Pigments play a critical role in these alternative technologies. New pigments, for such applications, allow coatings manufacturers to make the transition more easily and effectively.

Finally, how pigment users make the transition to alternative pigments or alternative technology and the level of support that pigment suppliers must provide.

REGULATIONS, REGULATIONS, REGULATIONS

The regulatory environment in the U.S. is already a very crowded place. There is the Coalition of New England Governors, and Super-fund Amendment and Reauthorization Act Title Ill: Sec. 313, Proposition 65, the Safe Drinking Water Act, the Clean Air Act, and

the Toy Safety Standard. The pace of regulation continues at breakneck speed. In the U.S. in 1991, 500 separate pieces of legislation involving regulation of solid waste, were introduced at the Federal, state and municipal level. However, only 77 became law.

While regulations have made doing business more difficult and costly, they also create opportunities. Opportunities to develop new technology and to differentiate a supplier from its competitors. This is the one common thread that weaves itself through each of these, and other, success stories.

REPLACEMENTS FOR LEAD CHROMATE PIGMENTS

Use of chrome yellow and moly orange declined drastically during the 70's and 80's mainly due to reformulation in publication printing and consumer and automotive OEM paint applications. The pace of reformulation slowed during the mid-80's but renewed activity started in the 1988/89 period. By this time, CONEG was already visible on the horizon and ink, paint and plastic customers began to actively seek alternatives to lead-based pigments.

One of the last bastions of lead chromate use in packaging ink was in bread bags. It was used because it was inexpensive, bright, opaque, resistant to fats and oils in the bread and did not migrate through the plastic film. The ink was printed on the outside of the bag so contact with the bread was not an issue. One of the largest producers of ink for this application came to us and other pigment suppliers for an alternative. After lab trials, press trials and discussions with the printers and the bread producers, the solution they selected for replacing Medium Chrome Yellow is Pigment Yellow 55 (AAPT). Several modifications were made to the pigment to ensure that the desired level of opacity was

achieved and a liquid ink test was made part of the quality control protocol for the pigment. Prior to this application, virtually no Yellow 55 was used in the U.S. in printing ink.

Another area of active interest for chromate pigment replacement is vinyl screen and specialty gravure inks. The performance requirements in these applications are a bit more demanding than those for packaging. The pigments used must have better lightfastness and chemical resistance than those normally used for packaging. For example, a pigment used in a vinyl flooring ink must have lightfastness of six or better on a Blue Wool Scale and must be resistant to highly alkaline pH cleaners like TOP JOB and Mr. CLEAN. Most diarylide yellows do not have the required lightfastness and metal precipitated azo reds would not withstand repeated exposure to household cleaners.

The solution for flooring inks and for a growing number of vinyl ink applications is MIXED AZO's. These products are a blend of organic pigments designed to closely approximate the shade of LIGHT and MEDIUM CHROME YELLOW and MOLY ORANGE. They exhibit excellent chemical resistance, are highly saturated and provide the required lightfastness and opacity. These products are also used in industrial coatings applications.

Recently, we were invited by a major producer of plastic automotive components to come in to tell what we knew about replacing encapsulated chromes and molys. We were reluctant to do so until we talked to our customer, the concentrate manufacturer who sells to the component maker, and obtained his support. After several pilot trials the solution that was selected consisted of a palette comprised of isoindolinone yellow and orange, and quinacridone and diketo-pyrrolo-pyrrol reds. Not only does such a palette

provide the required color coverage, the pigments also provide the required heat stability, and ease of processing.

Pigments	Heat Stability, F 5 min. Dwell	Lightfastness BWS Rating
Yellow 109	550	8
Yellow 110	550	8
Orange 61	550	7.5
Red 254	575	8
Violet 19	550	8

Blue Wool Scale (BSW) 8 = Excellent, 1 = Poor

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BARIUM REPLACEMENT

Ever since we the state of Florida passed legislation that required use of barium-free pigments on all merchandise bags, growing numbers of package buyers have been

pigments. That means no Red Lake C (Pigment Red 53.1); no Clarion Red (Pigment Orange 46); no Ba 2B Red (Pigment Red 48.1) and no Barium Lithol (Pigment Red 49.1).

million of these pigments were consumed in 1991 in the U.S. Also affected are pigments in which barium sulphate is used as an extender and to control strength and dispersion.

economy they provide. Alternatives do exist however and for specific applications work

very well. Very often combinations of pigments are required to match the shade of specific barium-based pigments.

Pigment Red 2 (Naphtol) is a very effective barium-replacement pigment. It is coloristically similar to Red Lake C and can be used as the foundation for blends to match Clarion Red and Ba 2B Red. Another naphthol pigment used is Pigment Red 22. We find that Red 2 is far superior to Red 22 for a variety of reasons:

It is more lightfast and soap and alkali resistant than Red 22 and Ba-based pigments.

It is 15-20% stronger than Red 22 and therefore is more economical to use.

*Provides better transparency than Red 22.

Summary of Resistance Properties:

Resistance to:	P.R. 2	P.R. 22	P.R. 53.1
Light, Fulltone	6	6	3
Light, Tint	4	1	2
Alkali	5	4	2
Soap	4	4	1
Alcohol	4	2	5
Wax	3	3	4
Fats	2	1	4

Lightfastness ratings: BSW (Blue Wool Scale), 1 = poor, 8 = excellent.

Resistance ratings: IS0 Gray Scale, 1 = poor, 5 = excellent.

Several pigments, notably Pigment Orange 34 (pyrazolone) and Pigment Red 4 (chlorinated para) are very effective blending pigments when used with Red 2. The exact rations will vary depending upon the application and the pigment being matched but in general the following blends provide a good starting point formulation:

Clarion Red	90/10 Orange 34/Red2
Red Lake C	60/40 Red 4/Red2
Ba 2B	90/10 Red 4/Red 2

Several liquid ink producers successfully sue Red 2 and Red 4. Reformulation of the ink was necessary in order to overcome the gloss deficiency associated with use of these alternative pigments. Approval did not come overnight. It came only after all of the parties, pigment and ink manufacturers, the printers, and the advertisers, understood the compromises and advantages involved.

CADMIUM REPLACEMENT

Cadmium replacement has become a particularly hot issue especially in plastics applications. It is not yet possible to replace ALL cadmium-based pigments in ALL very high temperature applications such as engineering plastics and nylon. However, for a large number of vinyl, polyolfin and certain ABS applications organic pigments with the requisite heat stability and saturation are doing the job once performed by cadmiums.

Walk down the aisle of your friendly neighborhood supermarket or toy store. Many of the containers and toys have been formulated away from cadmium colors to organics. Selection of the “correct” alternative pigment depends upon the performance criteria required and the processing temperatures involved.

LISTING OF SOME SUCCESSFULLY USED CADMIUM REPLACEMENTS:

Pigment Name	Chemical Type	Heat Stability, F
Yellows:		
Pigment Yellow 109	lsoindolinone	550
Pigment Yellow 110	lsoindolinone	550
Pigment Yellow 95	Azo condensation	525
Pigment Yellow 93	Axo condensation	500
Pigment Yellow 62	Azo complex	500
Pigment Yellow 17	Diarylide	450
Oranges:		
Pigment Orange 61	lsoindolinone	550
Pigment Orange 64	Azo Coupling	550
Reds:		
Pigment Red 254	DPP	575
Pigment Violet 19	Quinacridone	550
Pigment Red 202	Quinacndone	575

As recently as a few years ago there really wasn't much demand for high performance yellow and red organic pigments in high temperature plastics applications. Virtually all performance properties were satisfied by cadmium pigments. Why use a $40 er pound pigment when one that cost only $10 or $15 per pound worked just fine? Today, the demand for high performance organic replacements is growing rapidly due to regulation. Despite their high unit cost many plastics compounders report that they can achieve the same or better value with high performance organic pigments than they did with cadmiums.

The adage “Necessity is the Mother of Invention” certainly applies to the reds will show considerable color change at temperatures above 550 F. This restricts their magenta was introduced that provides compounders with an alternative to cadmium deep reds.

Typical Heat Resistance Data for New Quinacridone Magenta

ABS {DOW 342), 5 minute dwell

	Delta E		
	500F	55OF	6OOF
New QA Magenta	0.61	1.29	0.95
“Old” QA Magenta	1.70	2.05	3.15
Mercadium Dark Red	1.62	1.35	4.10

POLYCARBONATE (LEXAN), 5 Minute Dwell

	600	680F	715F
New QA Magenta	0.61	1.19	1.35
“Old” QA Magenta	0.43	2.69	4.88
Mercadium Dark Red	2.35	1.23	7.30

NYLON (B-300), 5 Minute Dwell

	550F	6OOF	650F
New QA Magenta	0.41	1.99	1.92
“Old” QA Magenta	1.86	3.33	4.53

PRODUCTS FOR HIGH SOLIDS SOLVENT AND WATER-BORNE COATINGS

During the last five years coatings manufacturers and raw material suppliers have been increasingly restricted by environmental regulations aimed at reducing the level of Volatile Organic Compounds (VOC) in paint formulations worldwide. Atmospheric VOC emissions from automotive vehicle manufacture have been estimated at 350,000 tons, worldwide, according to a 1989 article in JOCCA (Vol. 4, Pg. 139). This large quantity of organic solvents has forced the industry to develop higher solids coatings via changes in polymer architecture and/or pigment surfaces.

Pigment manufacturers have expended considerable R&D effort on surface modification of existing pigments so that they will provide the desired rheology and coloristic performance in such systems. For example, one can take an opaque Quinacridone Red Y, apply a specific surface treatment, and produce a product that exhibits almost newtonian flow in high solids acrylic paint.

System: High Solids Acrylic
30.9% Pigment, Pigment to Binder ratio = 1.25

Shear Rate	Surface Treated Red Y	Conventional Red Y
10 rmp	520 cps	15720 cps
50	328	4520
100	272	2640
Millbase yield	82%	65%
Gloss	84	66
DOI	98	87

As one can see from the data the surface treated product provides the required viscosity profile for use in high solids solvent systems,

lndanthrone Blue (Pigment Blue 60) is a high performance transparent pigment particularly well suited for automotive finishes. However, the small particle size essential for transparency and two tone characteristics is responsible for high viscosity and poor flow in high solids systems. By applying a specific surface treatment we obtain a product that has better flow and is stronger and more transparent because the small particles no longer flocculate as in the un-treated product.

System: High Solids acrylic
10% Pigment, Pigment to Binder ratio = 0.5

Shear Rate	Surface Treated Blue 60	Conventional Blue 60
10 rpm	480 cps	6120 cps
20	300	3540
50	184	1670'
Tint Strength	132	100
Transparency	100	89

These and other surface modified pigments form part of the palette used by automotive color stylists in Detroit. Other products are currently under development.

Manufacturers of WOOD STAINS and related products are also actively working on reduced-VOC systems. A typical solvent-based NGR (non-grain raising) stain may contain as little as 2% to 5% solids with the remainder being comprised of alcohol, hydrocarbon and glycol solvents. The colorants used in wood stains include organic

pigments for shading earth colors such as Sienna and Burnt Umber, and dyes. The dyes fall into three broad classifications: Acid dyes, Spirit dyes and Solvent Soluble dyes. None of them work well in water-based and combination water-solvent systems. Spirit and Solvent Soluble types are insoluble and acid dyes are extended with adulterating agents which detract from the stability and quality of the final stain.

Recently, a new range of dyes, supplied in solution form, were developed and commercialized. Most large and medium size stain manufacturers have already begun to use these products in water/solvent stains. They report excellent results and anticipate using greater quantities of these products as customer approvals are received.

These new products are supplied as highly concentrated solutions with either 1-methoxy-2-propanol or 1 -ethoxy-2-propanol as the main solvent. The products provide the following advantages to stain producers:

*Ready to use form

*Better lightfastness than Acid and Spirit dyes

*Improved resistance to acid-catalyzed, urethane, polyester and nitrocellulose top-coats than Acid or Spirit dyes.

*Salt free.

*Broad solvent compatibility, including:

Alcohols	Glycol Ethers
Ketones	Alipatic Hydrocarbons
Esters	Aromatic Hydrocarbons
Glycols	Water

PRODUCT REPOSITIONING

Replacing a pigment that is working well is something that formulators do not relish. Any change involves risk ("Will the final product satisfy the customer?" "Will my competitor come up with something better?") and expense.

How do you make the transition to environmentally acceptable pigments? How do you help your customer make the transition? It is not easy. The road to success if replete with curves and potholes. We have found the following "guidelines" essential in assisting our customers:

*Be persistent. Success does not come overnight.

*Recognize that every situation is unique. Two customers trying to replace the same pigment will have different concerns and priorities.

*Involve your customer's customer, if possible. The transition takes place much more quickly and easily when everyone in the value chain (supplier, user, customer) supports the change.

*Rely upon your suppliers to provide you with information on environmental issues and regulations, their implementation and the potential effect upon your business. Our Product Safety group works closely with Marketing and our customers.

*Use your pigment supplier as a technical resource. For information on suitable replacement pigments, for laboratory and color matching work, for process development recommendations, for additive package

recommendations, etc.

*Be proactive in developing environmentally sound products rather than being forced to react by regulations or by your competitor.

CONCLUSIONS

In summary, there are really three main points concerning ENVIRONMENTALLY ACCEPTABLE PIGMENTS that I would like you to take away with you today.

1. They are a Reality for a growing number of pigment users.

2. They represent an opportunity to establish COMPETITIVE ADVANTAGE.

3. They are the subject of intensive R&D and technical support by pigment manufacturers.