Role of Mildewcide in Yellow Discoloration of Latex Paints

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Paint formulators must take into account many factors including, but not limited to, ease of application, durability, scrub resistance, fading, and discoloration when formulating a new paint. Although discoloration can be caused by many factors including tannin-related stain bleeding, mildew-related sap staining, fading due to sunlight, yellowing due to alkyd modification, and interactions between colorants and pigments, clay, and other filler pigments, this article specifically explores the effect of mildewcides on yellowing.[1-4]

The effect of mildewcides on yellowing in latex paints has been an ongoing concern for paint manufacturers. Mildewcides and their interactions with various paint ingredients including certain in-can preservatives, binders, pigments, and clay are a known phenomenon.[5] Through experience, paint companies have developed formulations to optimize the efficacy of mildewcides and minimize their adverse effects in paints. Recently, formulators have been facing a new challenge to produce low- or zero-VOC paints.[10] These lower- or zero VOC paint requirements came about due to legislation such as the South California Air Quality Management District law (SCAQMD) as well as the public's increasing concerns for the environment.[11-13] Lowering VOC content can affect application characteristics, and presents the new challenge to minimize changes in the performance properties of the coatings including yellowing in low- or zero-VOC formulations. New ingredients that may be incorporated to achieve these modified VOC goals may include

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low- or zero-VOC reactive coalescent agents (RCA) such as Archer™ RC (ADM) , or low-VOC formulations of mildewcides such as Fungitrol™ 820 (ISP Chemicals Inc).[9,10,12] Mildewcides that have been in use for certain types of paints in the past may not be suitable in new lower or zero-VOC formulations. To date, most studies have examined only the effect of these changing ingredients on the film formation and the application properties of these low- or zero-VOC paints.[8,12,13] We undertook an extensive evaluation to study the effects of various mildewcides in several low-VOC paint formulations. We report in this article our significant findings from more than 300 paint formulations tested with all possible mildewcide options.

MATERIALS AND METHOD

Paint Formulations Tested

Generic Flat Paint Formulation: The Flat Paint formulations were prepared using four different commercially available binders including acrylic, vinyl versatate, and vinyl acetate-ethylene from different manufacturers and two different commercially available coalescent agents. These paints contained total PVC of 44.9% with volume solids of 36.3% with calculated VOC of 100 gm/L.

Generic Semi-Gloss Formulations: The Semi-Gloss Paint formulations were prepared using four commercially available binders including acrylic and acrylic-styrene latex from different manufacturers and two different commercially available coalescent agents. These paints contained a total PVC of 22.0% and volume solids of 34.0% with calculated VOC of 150 gm/L.

Mildewcides Tested

The single active and combination mildewcides listed in *Table* 3 are commercially available products used today in paint formulations, and were evaluated in this study since they are likely to be used as a starting point in the new low- or zero-VOC coatings formulations.

Among the single active chemistries, iodo-propargyl butyl carbamate (IPBC) chemistries are typically known to contribute to yellowing in paints.[4] New and improved formulations have been developed that are low or zero VOC, as well as "less yellowing" formulations. These new IPBC formulations were tested in these studies. *Table* 3 also lists the combination and dispersion type mildewcide formulations that are becoming increasingly popular due to their broad spectrum of activity, and their effectiveness against both algae and fungi. With the increased popularity of these blended biocides, it is very likely they will be used in low- or zero-VOC formulations. Therefore, they are included in this study.

Table 1—VOC Regulations for Latex Paints

Paint Type	U.S. EPA (1999)	SCAQMD[a] (Rule 1113)	OTC[b]	CARB[c] (1/2003)
Flat (Interior and Exterior)	250	100 (50 by 7/2008)	100	100
Semi-Gloss	380	150 (50 by 7/2006)	150	150
High-Gloss	XXX	150 (50 by 7/2006)	250	250

(a) SCAQMD—South Coast Air Quality Management District.
(b) OTC—Ozone Transport Commission: Comprised of 12 northeastern U.S. states.
(c) CARB—California Air Resources Board

Dosing and Drawdown of Paints

Prepared paints were post-dosed with the appropriate level of mildewcide and mixed thoroughly. Dosed paints were allowed to equilibrate for 24 hr before preparing the drawdowns. Drawdowns of each sample (three-mil thick wet) were prepared using a 3 ml Bird applicator on plain white unlaquered Leneta chart paper (The Leneta Company). Coated chart papers were allowed to air dry at room temperature for 24 hr before testing.

Color Measurement

Color measurements were performed on drawdown samples that either remained at room temperature,

Table 2—Binders and Coalescent Agents Used in This Study

Binder	Binder Type	Manufacturer
Flats:		
Airflex™ EF811	VAE	Air Products Polymers LLP
NeoCar™ 2535	VA VEOVA	Union Carbide Corporation
Rhoplex™ ML 200	Acrylic	Rohm and Haas Company
EPS™ 2734	Acrylic	EPS/CCA
Semi-Gloss:		
Rhoplex SG-30	Acrylic	Rohm and Haas Company
Rhoplex SG-20	Acrylic	Rohm and Haas Company
Rhoplex 2200	Styrene acrylic	Rohm and Haas Company
Optive™ 130	Acrylic	BASF Corporation
Coalescent Agents:		
Texanol™	Non-reactive coalescing agent (NRCA) ester ethanol	Eastman Chemical Company
Archer RC™	Reactive coalescing agent (RCA) corn oil esters	ADM Chemical Company

Figure 1—Yellowing study in flat paints using non-reactive coalescing agent (NRCA) in room temperature exposed films.

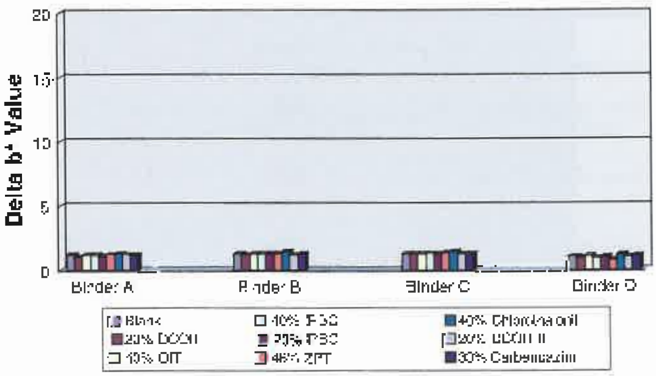
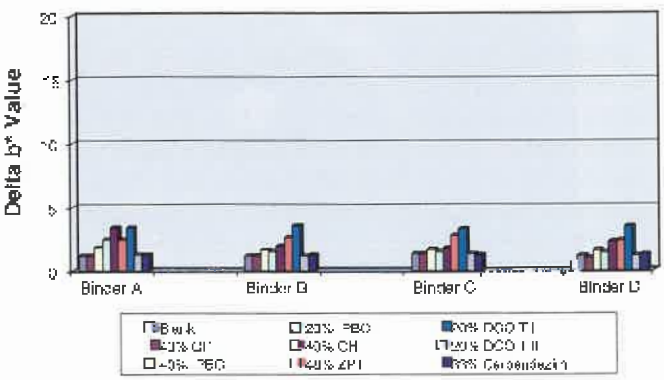


Figure 2—Yellowing study in flat paints using NRCA in 24-hr UV exposed films.



were exposed to 24 hr of UV light, or were sprayed with Krylon Kamar™ Varnish 1312 and exposed to UV light for 4 hr.[6,7] In the Krylon Method, drawdowns were sprayed with Krylon Kamar Varnish 1312 (Krylon Products Group) for 1 min and allowed to air dry. Drawdowns were sprayed for a total of 5 min. After drying, samples were exposed to UV light for 4 hr. Color was measured using the X-Rite Colorimaster 8400. Results of the *b values are reported in the graphs.

RESULTS AND DISCUSSION

Table 1 shows the VOC regulations for latex paints in effect at the time of this experiment. Subsequent SCAQMD regulations will require even lower VOCs (50 gm/L) for flat and semi-gloss paints. However, for the majority of the U.S., the current VOC level for flat paint is 100 gm/L and 150 gm/L for semi-gloss paint, which are the levels used for this screening study. We selected several commercially available binders and coalescing agents (see *Table* 2). Coalescing agents included non-reactive coalescing agents (NRCA) such as ester alcohols, and reactive coalescing agents (RCA) based on corn oil esters promoted and tested for low-VOC formulations. *Table* 3 lists mildewcides tested for their effects on various formulations for yellowing potential in dry films. Mildewcides are one of the key additives in a paint formulation that can affect the dry film properties and appearance. In *Table* 3, the mildewcide categories tested are classified as three sub groups: I—single active mildewcide; II—various formulations of the IPBC mildewcide that are new improved non yellowing or new low-VOC formulations to complement the new low-VOC regulations for paints; and III—commercial combinations or physical blends. The

Figure 3a—Effect of single active mildewcide on film yellowing in flat paints based on four binders using NRCA (Krylon Clearcoat/4-hr UV method).

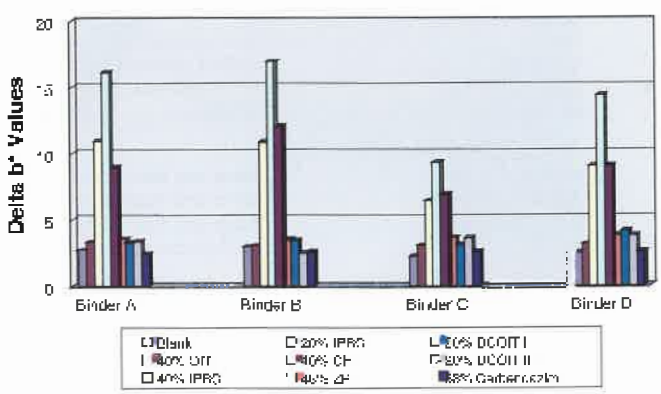


Figure 3b—Effect of single active mildewcide on film yellowing in flat paints based on four binders using reactive coalescing agents (RCA) (Krylon Clearcoat/4-hr UV method).

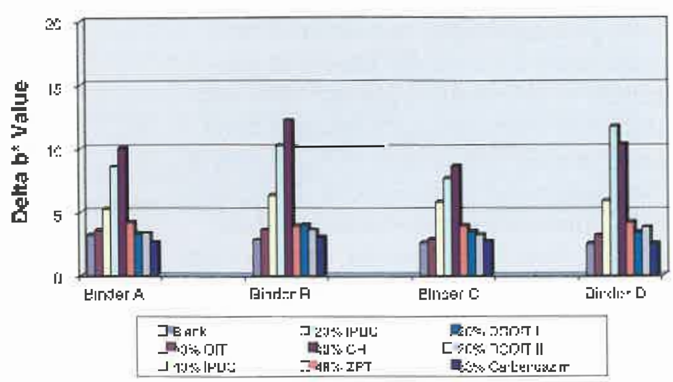


Figure 4a—Effect of single active mildewcide on film yellowing in semi-gloss paints based on four binders using NRCA agents (Krylon Clearcoat/4-hr UV method).

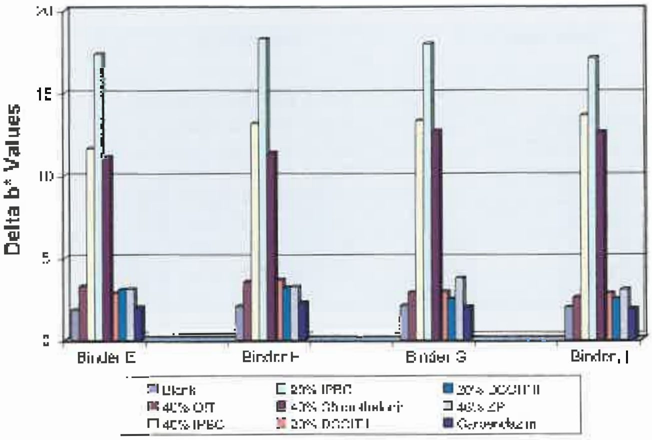


Figure 4b—Effect of single active mildewcide on film yellowing in semi-gloss paints based on four binders using RCA agents (Krylon Clearcoat/4-hr UV method).

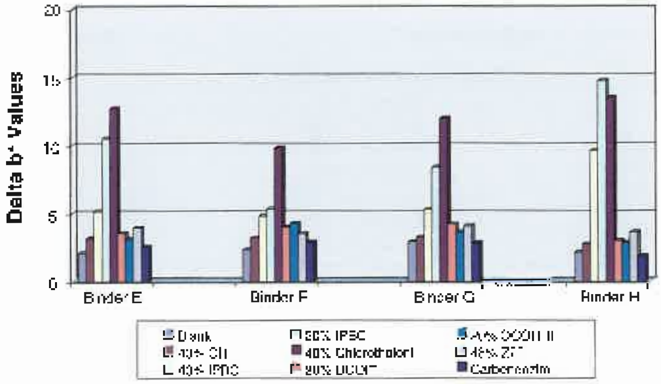


Figure 5a—Effect of mildewcide formulations on yellowing of flat paints based on NRCA IPBC formulations (Krylon Clearcoat/4-hr UV method).

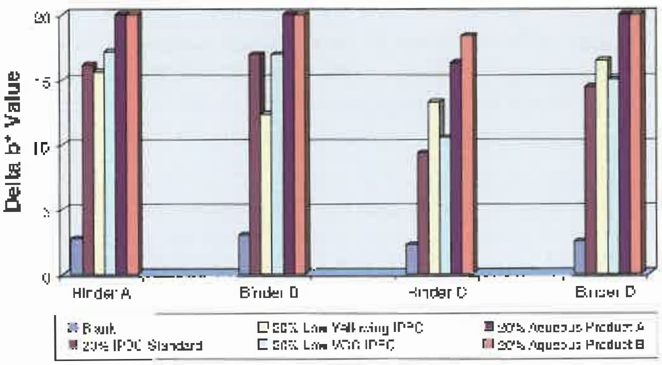


Figure 5b—Effect of mildewcide formulations on yellowing of flat paints based on RCA IPBC formulations (Krylon Clearcoat/4-hr UV method).

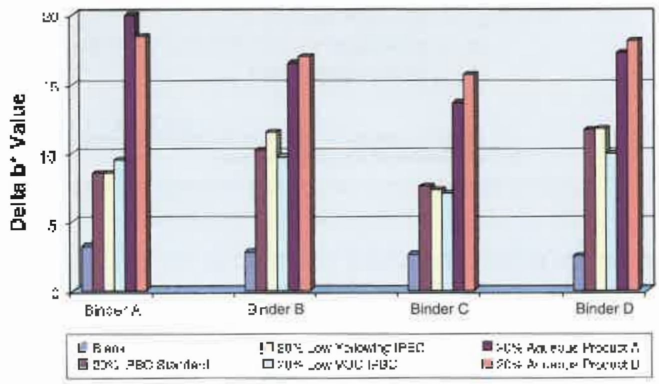


Figure 6a—Effect of mildewcide formulations on yellowing of semi-gloss paints based on NRCA agents (Krylon Clearcoat/4-hr UV method).

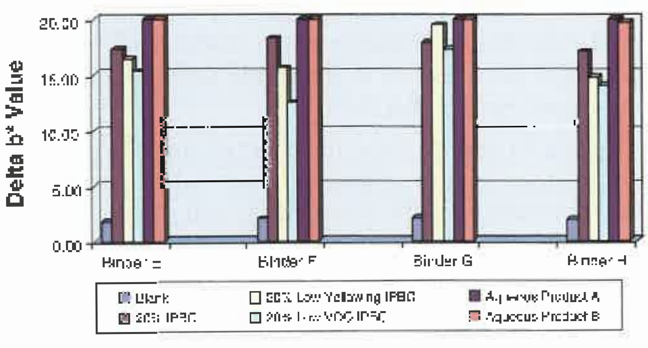


Figure 6b—Effect of mildewcide formulations on yellowing of semi-gloss paints based on RCA (Krylon Clearcoat/4-hr UV method).

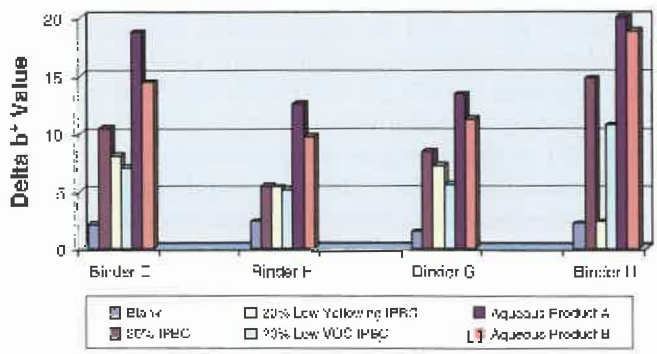


Table 3—Mildewcides Used and Their Abbreviations

Mildewcide Type		lb/100 gal	Code Name	Manufacturer
I. Single Active Mildewcide				
1.	Skane™ M-8	3.0	40% OIT	Rohm and Haas Company
2.	Rozone™ 2000	5.57	20% DCOIT I	Rohm and Haas Company
3.	Rocima™ 200	5.57	20% DCOIT II	Rohm and Haas Company
4.	Carbendazim	0.9	33% Carbendazim	Rohm and Haas Company
5.	Polyphase™ AF1	1.6	40% IPBC	Troy Chemical Company
6.	Polyphase P-20T	6.0	20% IPBC	Troy Chemical Company
7.	Zn Omadine™	8.0	48% ZPT	Arch Chemical Company
8.	Nuocide™ 404D	10.0	40% CH	ISP Chemicals Inc.
II. Single Active IPBC Versions Comparison				
1.	Polyphase P-20T	6.0	20% IPBC	Troy Chemical Company
2.	Fungitrol™ 720	6.0	20% Low yellowing IPBC	ISP Chemicals Inc.
3.	Fungitrol 820	6.0	20% Low VOC IPBC	ISP Chemicals Inc.
4.	Experimental	6.0	20% Aqueous Product A	Rohm and Haas Company
5.	Generic product	6.0	20% Aqueous Product B	Source X
6.	Polyphase CST	6.0	20% Aqueous Product C	Troy Chemical Company
III. Blended Dispersion Products				
1.	Polyphase 678	8.0	I/C[a]	Troy Chemical Company
2.	Polyphase 663	10.0	I/C/D	Troy Chemical Company
3.	Rocima™ 63	10.0	O/C/D	Rohm and Haas Company
4.	Rocima 355	8.5	I/DO	Rohm and Haas Company
5.	Rocima 65	10.0	DO/C/T	Rohm and Haas Company
6.	Zn Omadine™ ZOE	8.0	ZPT	Arch Chemicals Company
7.	Nuocide™ 2010	8.0	I/CH	ISP Chemicals Inc.
8.	Nuocide 2002	8.0	CH/T	ISP Chemicals Inc.
9.	Acticide™ PM	10.0	CH/D	THOR Chemical Company
10.	Acticide PA	10.0	O/CH/D	THOR Chemical Company
11.	DCOIT/chlorothalonil	1:1[b]	DO/CH	Rohm and Haas Company

(a) I = IPBC; C = Carbendazim; DO = DCOIT; O = OIT; CH = Chlorothalonil; T = Triazine; D = Diuron; ZPT = Zinc Pyrithione.
(b) Experimental blend 1000:1000 (ppm) ratio.

latter are getting increasing attention in the paint industry due to their claim of broad spectrum activity.

Dry film yellowing is a phenomenon normally observed in films exposed to light in indoor or outdoor conditions. In many cases, observations of the yellowing phenomenon are a challenge and are not reproducible in defined laboratory conditions. This may be because the varieties of formulations and the interactions of many ingredients in a paint formulation may vary from condition to condition. For this study, we screened three test methods that provide consistent reproducible yellowing of dry films.

Figure 1 shows that flat paint dried at room temperature shows no color development. The same paint film when exposed to UVB (313 nM) light for 24 hr, showed color development that measures up to delta b of 3–4 (*Figure* 2). A greater degree of yellowing was noted in paints containing either IPBC or chlorothalonil than in paints containing DCOIT or other mildewcide. This color development in UV exposed film was more pronounced in a method where the surface of the film is sealed with a clear coating of a non-yellowing varnish.[7] In these sealed dry films, UV exposure of just 4 hr was sufficient to trap the yellow chromophore for measurement. With this method, it can be clearly seen in the flat paint formulation (*Figures* 3a–3b) that IPBC and chlorothalonil-containing paints were the most yellowed. DCOIT, ZPT, and Carbedazim yellowed the least. The yellowing of these films was consistent with all types of binder tested. The data also shows that when a non-reactive coalescing agent was substituted with a reactive coalescing agent, the relative degree of yellowing was decreased but the trend was that IPBC and chlorothalonil yellowed consistently (*Figures* 3a–3b). Interestingly, DCOIT-based mildewcide has been implied occasionally as cause for yellowing under certain conditions; however, when investigated further, there were other factors found in the formulation that influenced the discoloration.[5]

Figures 4a and 4b show the effect of single active mildewcides on film yellowing in semi-gloss paints. In these formulations, the actives IPBC and chlorothalonil were again the most yellowing and DCOIT and other mildewcides showed the least yellowing as tested by the accelerated test method. Again, the formulations containing the NRCA showed a higher degree of yellowing

Figure 7a—Effect of combination mildewcides on film yellowing in flat paints using Texanol as the coalescent agent (Krylon Clearcoat/4-hr UV method).

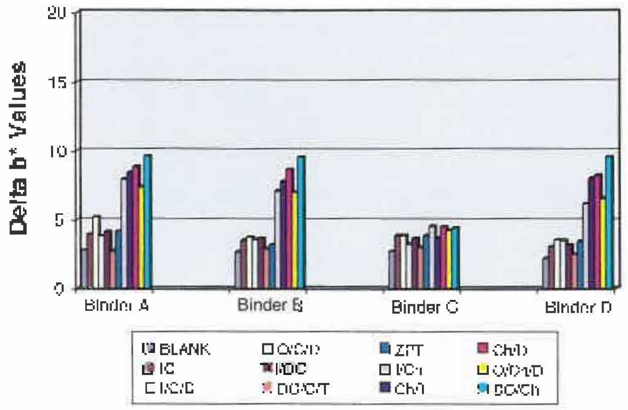
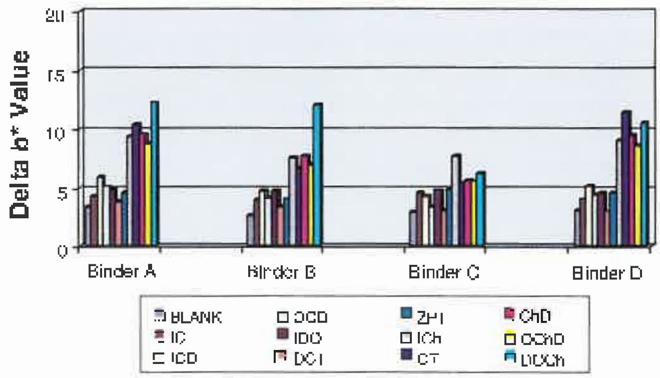


Figure 7b—Effect of combination mildewcides on film yellowing in flat paints using Archer RC as the coalescent agent (Krylon Clearcoat/4-hr UV method).



than the paint films containing RCA. Also noted was the influence of the formulations of a mildewcide product on the degree of yellowing. The 20% IPBC-based product tested in these evaluations exhibited more yellowing than the 10% IPBC product. There are several new and improved IPBC-based mildewcides available for paint formulators to consider while reformulating their paints for lower VOC compliance. These IPBC products are formulations with improvement on color development or low-VOC products.

We also studied the various IPBC products available on the market along with two experimental aqueous formulations for their influence on yellowing in the various low-VOC paints. As shown in *Figures* 5a and 5b, the standard 20% IPBC formulations yellowed significantly in a flat paint based on NRCA while the paint based on RCA exhibited reduced yellowing. Similar observations were noted for semi-gloss paints (*Figures* 6a and 6b). An interesting observation in this study was that the IPBC formulations that are promoted as low-yellowing and low-VOC versions showed the most yellowing. This observation is notable since for the low-VOC paint regulations attempts are being made to reduce VOC levels in any additive that would help eliminate VOC contribution to the final formulation.

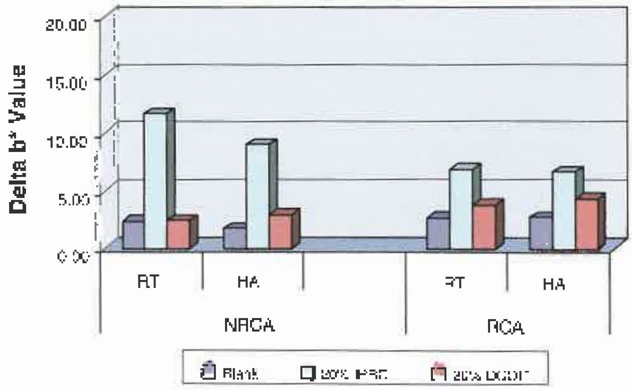
We also evaluated several combination mildewcides in all paint formulations, using the two coalescing agents, NRCA and RCA. As shown in *Figures* 7a (NRCA) and 7b (RCA), the blends that contained chlorothalonil were the most yellowing in these tests. Again, the degree of yellowing varied depending upon the binder type and coalescent used.

The heat age stability and contribution of any film defects of any mildewcide is a question often asked when testing in new formulations, particularly in low-VOC formulations. We evaluated semi-gloss paints by heat aging the paints at 60°C for 10 days. Drawdowns were made and subjected to 4 hr UV with clear sealing on them. *Figure* 8 shows that in our semi-gloss paint formulations, paint made with NRCA coalescent yellowed more than paints formulated with RCA coalescent. Again, we noted that IPBC-containing paints yellowed more than DCOIT-based paints.

CONCLUSION

Reformulation of paints to comply with new low-VOC regulations is a task being undertaken by many paint companies. The paint manufacturers have the huge job of qualifying many new raw materials such as low-VOC binders, improved coalescent agents, surfactants, and other additives like old and new mildewcide formulations. This screening of 300 paints for yellowing potential will hopefully facilitate this huge task for

Figure 8—Comparison of room temperature and heat aged semi-gloss paint containing IPBC and DCOIT mildewcides.



paint manufacturers. In summary, this study shows that the potential of a dry film to yellow is greatest in formulations containing chlorothalonil or IPBC-based mildewcides. Our data also indicates that the formulation of IPBC-based mildewcide can play a significant role in yellowing. DCOIT-based mildewcides showed the least yellowing. In addition, effects of heat aging paints appear to be negligible compared to formulation effects (coalescent and mildewcide).

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