Role of Mildewcide in Yellow Discoloration of Latex Paints

by Lakshmi Sadasivan, Roger C. Montemayor, and Judith N. Varner
Rohm and Haas Company

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 alkyl modification, and interactions between colorants and pigments, clay, and other filler pigments, this article specifically explores the effect of mildewcides on yellowing.¹ ²

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.³ Through experience, paint companies have developed several 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.⁴ 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.⁵ ⁶ ⁷ 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.

Materials and Method

Paint Formulations Tested

Generic Flat Paint Formulations: The Flat Paint formulations were prepared using four different commercially available binders including acrylic, vinyl versate, 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 g/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 g/L.

Mildewcides Tested

The single 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, tode-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 those 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.

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 mil Bird applicator on plain white unlaskerized 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 1—VOC Regulations for Latex Paints

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat (Interior and Exterior)</td>
<td>250 (50 by 7/2006)</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Semi-Gloss</td>
<td>380 (50 by 7/2006)</td>
<td>150</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>High-Gloss</td>
<td>XXX (50 by 7/2006)</td>
<td>250</td>
<td>250</td>
<td></td>
</tr>
</tbody>
</table>

* SCAQMD—South Coast Air Quality Management District.
* OCA—Sacramento Air Resources Board.
* CARB—California Air Resource Board.

Table 2—Binders and Coalescent Agents Used in This Study

<table>
<thead>
<tr>
<th>Binder Type</th>
<th>Manufacture</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAE</td>
<td>Air Products-Polymer LLC</td>
</tr>
<tr>
<td>VA-VEDAX</td>
<td>Union Carbide Corporation</td>
</tr>
<tr>
<td>Acrylic</td>
<td>Rohm and Haas Company</td>
</tr>
<tr>
<td>EFS 2724</td>
<td>Eka Chemical Company</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Semi-Gloss</th>
<th>Manufacture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic</td>
<td>Rohm and Haas Company</td>
</tr>
<tr>
<td>Acrylic</td>
<td>BASF Corporation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coalescent Agents</th>
<th>Manufacture</th>
</tr>
</thead>
<tbody>
<tr>
<td>tode-propargyl butyl carbamate</td>
<td>Eka Chemical Company</td>
</tr>
<tr>
<td>reactive coalescing agent (RCA)</td>
<td>Rohm and Haas Company</td>
</tr>
<tr>
<td>corn oil esters</td>
<td>Eka Chemical Company</td>
</tr>
</tbody>
</table>

Prepared at the Federation of Societies for Coatings Technology’s 2006 FallCoat Conference, November 1-3, 2006, New Orleans, LA.


Role of Mildewcide in Yellow Discoloration of Latex Paints

by Lakshmi Sadasivan, Roger C. Montemayor, and Judith N. Varner
Rohm and Haas Company* 

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 may be caused by many factors including tannin-related stain bleeding, mildew-related sap staining, fading due to sunlight, yellowing due to alkyl modification, and interactions between colorants and pigments, clay, and other filler pigments, this article specifically explores the effect of mildewcides on yellowing.1,2,3

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.1 Through experience, paint companies have developed techniques 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.6 These lower- or zero-VOC paint requirements came about due to legislation such as the South California Air Quality Management District (SCAQMD) as well as the public’s increasing concerns for the environment.1,2,3 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 low- or zero-VOC reactive coalescent agents (RCA) such as Archer* RC (AD4), a low-VOC formulations of mildewcides such as Fujifilm® 820 (SP Chemicals Inc.), and 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.1,2,3,4,5 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 versatic, 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 g/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 total PVC of 22.0% and volume solids of 34.0% with calculated VOC of 150 g/L.

Mildewcides Tested

The single active and combination mildewcides listed in Table 1 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, penta- or trimethyl benzyl carbamate (IPBC) chemistries are typically known to contribute to yellowing in paints.4 New and improved formulae have been developed that are low or zero VOC, as well as “less yellowing” formulations. These new IPBC formulations were tested in this study. 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.

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 h before preparing the drawdowns. Drawdowns of each sample (three-inch thick wet) were prepared using a 3 ml Bird® applicator on plain white unlacquered Leneta chart paper (The Leneta Company). Coated chart papers were allowed to air dry at room temperature for 24 h before testing.

Color Measurement

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

Table 1—VOC Regulations for Latex Paints

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat (Interior and Exterior)</td>
<td>750</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Semi-Gloss</td>
<td>380</td>
<td>150</td>
<td>250</td>
</tr>
<tr>
<td>High-Gloss</td>
<td>XXX</td>
<td>250</td>
<td>250</td>
</tr>
</tbody>
</table>

*SCAQMD—South Coast Air Quality Management District.
**OSHA—Occupational Safety and Health Administration of the United States, U.S. Department of Labor.
***CARB—California Air Resource Board.

Table 2—Binders and Coalescent Agents Used in This Study

<table>
<thead>
<tr>
<th>Binder Type</th>
<th>Manufacturer</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Products Polymers LLC</td>
<td>Air Products Polymers LLC</td>
<td>Air Products Polymers LLC</td>
</tr>
<tr>
<td>Acrylic</td>
<td>Acrylic</td>
<td>Acrylic</td>
</tr>
<tr>
<td>Non-reactive coalescing agent (NBRA) enter ethylene</td>
<td>Non-reactive coalescing agent (NBRA) enter ethylene</td>
<td>Non-reactive coalescing agent (NBRA) enter ethylene</td>
</tr>
<tr>
<td>Reactive coalescing agent (RCA) corn oil esters</td>
<td>Reactive coalescing agent (RCA) corn oil esters</td>
<td>Reactive coalescing agent (RCA) corn oil esters</td>
</tr>
</tbody>
</table>

www.coatingsTech.org
were exposed to 24 hr of UV light, or were sprayed with Krylon Kamar® Varnish 1312 and exposed to UV light for 4 hr.12 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 ColorLasermaster 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 SCQMD regulations will require even lower VOCs (50 g/L) for flat and semi-gloss paints. However, for the majority of the U.S., the current VOC level for flat paint is 100 g/L and 150 g/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, propranolol, 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 subgroups: I—single active mildewcide; II—various formulations of the IPBC mildewcide that are now 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
were exposed to 24 hr of UV light, or were sprayed with Krylon Kamar® Varnish 1312 and exposed to UV light for 4 hr.** 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 Colorimeter 8400. Results of the *p* 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 g/L) for flat and semi-gloss paints. However, for the majority of the U.S., the current VOC level for flat paint is 100 g/L and 150 g/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 pretested 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 subgroups: 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.
latter are getting increasing attention in the paint in-
dustry due to their claim of broad spectrum activity.
Dry film yellowing is a phenomenon normally ob-
served in films exposed to light in indoor or outdoor
conditions. In many cases, observations of the yellow-
ing phenomenon are a challenge and are not repro-
ducible in defined laboratory conditions. This may be
because of the varieties of formulations and the interac-
tions of many ingredients in a paint formulation may
vary from condition to condition. For this study, we
screened three test methods that provide consistent re-
producible yellowing of dry films.

Figure 1 shows that flat paint dried at room tempera-
ture shows no color development. The same paint film
when exposed to DUV (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 DCCOT or other mildewcides. 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 measure-
ment. With this method, it can be clearly seen in the flat
paint formulation (Figure 3a–3c) that IPBC and
chlorothalonil-containing paints were the most yel-
lowed. DCCOT, ZPP, and Carbendazim yellowed the
least. The yellowing of these films was consistent with
all types of binder tested. The delta B 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 that IPBC and
chlorothalonil yellowed consistently (Figure 3a–3b).
Interestingly, DCCOT-based mildewcide has been
implied exceptionally as cause for yellowing under
several conditions; however, when investigated further,
there were other factors found as the formulation that
influenced the discoloration.8

Figure 4a and 4b show the effect of single active
mildewcides on film yellowing in semi-gloss paints. In
these formulations, the active IPBC and chlorothalonil
were again the most yellowing and DCCOT and other
mildewcides showed the least yellowing as tested by
the accelerated test method. Again, the formulations con-
taining the NRCA showed a higher degree of yellowing
than the paint films containing RCA. Also noted was the
influence of the formulations of a mildewcide product on
doing yellowing. The 20% IPBC-based product tested in
developing more yellowing than the 40% IPBC product. There are
several new and improved IPBC-based mildewcides
available for paint formulators to consider while re-
formulating their paints for lower VOC compliance.
These IPBC products are formulations with improve-
ment on color development or low-VOC products.

We also studied the various IPBC products available
on the market along with two experimental aqueous for-
mulations for their influence on yellowing in the
various low-VOC paints. As shown in Figures 5a and 5b,
the standard 20% IPBC formulations yellowed signifi-
cantly in a flat paint based on NRCA while the paint
based on RCA exhibited reduced yellowing. Similar ob-
servations were noted for semi-gloss paints (Figure 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 yel-
lowing. 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 de-
ge 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 30 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 yel-
lowed more than paints formulated with RCA coales-
cent. Again, we noted that IPBC-containing paints yel-
lowed more than DCCOT-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, surfac-
tants, and other additives like old and new mildewcides.
This screening of 300 paints for yellowing
potential will hopefully facilitate this huge task for

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).

Figure 8—Comparison of room temperature and heat aged semi-gloss
paint containing IPBC and DCCOT mildewcides.
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 TUV (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 IPC or chloroaluminium than in paints containing DCCOIT or other mildewcides. 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. 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 IPC and chloroaluminium-containing paints were the most yellowed. DCCOIT, ZPT, and Carbadox 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 IPC and chloroaluminium yellowed consistently (Figures 3a-3b). Interestingly, DCCOIT-based mildewcides have 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 active IPC and chloroaluminium were again the most yellowing and DCCOIT 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 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% IPC-based product tested in these experiments exhibited more yellowing than the 40% IPC product. There are several new and improved IPC-based mildewcides available for paint formulators to consider while re-formulating their paints for lower VOC compliance. These IPC products are formulations with improvement on color development or low-VOC products.

We also studied the various IPC 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% IPC 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 IPC 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 chloroaluminium were the most yellowing in these tests. Again, the degree of yellowing varied depending upon the binder type and coalescing 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 coalesced yellowed more than paints formulated with RCA coalescent. Again, we noted that IPC-containing paints yellowed more than DCCOIT-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 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 8 as the coalescent agent (Krylon Clearcoat/4-hr UV method).

Figure 8—Comparison of room temperature and heat aged semi-gloss paint containing IPC and DCCOIT 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).

ACKNOWLEDGMENTS

We wish to thank Linda Adamson for providing advice on selecting low-VOC paint formulations for this study, Eileen Warwick and Susan Gill for support and critical review of this manuscript, and Rohm and Haas Company for supporting the publication of this study. We also gratefully acknowledge the paint companies that provided us with raw materials in the form of binders, coalescent agents, and mildewcides.

References