

ORGANIC TITANATE

A New Additive for Solvent-Based Printing Inks

Overview

Dorf Ketal Tyzor[®] IAM, a new grade of titanate, offers improved performance in solvent-based flexographic and gravure printing inks. This document describes the overall advantages of Dorf Ketal Tyzor[®] titanates and zirconates and highlights the distinctive performance and environmental benefits Tyzor[®] IAM brings to the industry.

Tyzor[®] organic titanates and zirconates are adhesion promoters and cross-linkers that are essential additives for flexographic and gravure printing inks.

The unique properties of the Tyzor[®] products help to enhance the performance of printing inks in a variety of applications, specifically flexible packaging.

Flexible packaging has become an important component of product marketing. Packaging materials usually include a non-absorbing foil based on polyolefin (polyethylene, polypropylene, or co-extruded polypropylene), polyester, polyamide, cellophane, PVC, metallized plastic, or aluminum. Printing on these foils can help to motivate consumers to purchase products, provide information, and offer decorative enhancement.

Typical print platforms for flexible packaging are flexography and rotogravure processes that require specialized inks. The type of ink most often used contains nitrocellulose (NC) as the primary binder.

For flexographic and gravure package printing, Tyzor[®] titanates and zirconates help to improve the final product properties. This is achieved by the titanate or zirconate acting as a cross-linker for the binder and as an adhesion promoter between the ink and substrate, which provides the following benefits:

- Improved adhesion of the ink to the substrate
- Enhanced curing
- Improved chemical, solvent, and water resistance
- Enhanced heat resistance
- Decreased drying times or lower cure temperatures
- Increased lamination bond strength

Dorf Ketal is the industry pioneer and a global leader in producing organic titanates and zirconates, and is a proven worldwide supplier of these products for a variety of industrial applications.

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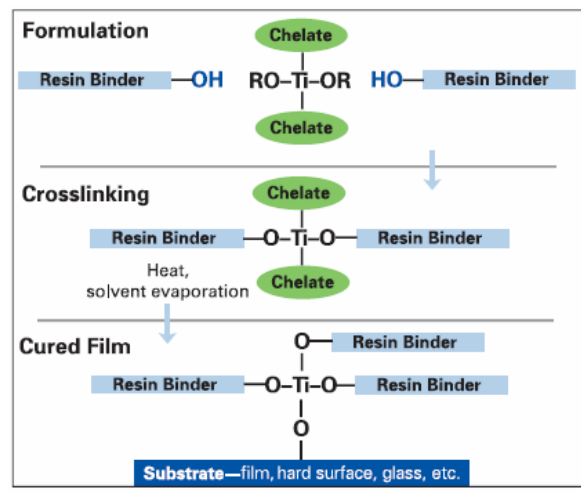
Formulation

Dorf Ketal Tyzor[®] titanates and zirconates are designed to work within existing ink systems. This section provides background information for achieving success in this application.

The binder must contain functional groups (e.g., -OH, -COOH) to achieve reaction with the titanate or zirconate. Possible binder systems include nitrocellulose (NC), polyvinylbutyral (PVB), cellulose acetobutyrate (CAB), and cellulose acetopropionate (CAP). The ink may also contain cobinders, such as polyamide (PA), polyurethane (PU), or plasticizers. All are prepared in an organic solvent or solvent mixture (such as ethanol, propanol and ethylacetate, etc.). The pigments provide coloration, but also can crosslink into the cured ink along with the binders and resins. Below is an example of a basic ink formulation containing a titanate additive.

Example of a Basic Formulation:	
Ethanol	21 pbw
Ethylacetate	21 pbw
Plasticizer	2 pbw
Pigment	30 pbw
PU Resin	8 pbw
NC Resin (35% a.i.)	16 pbw
Titanium Chelate	2 pbw
Total	100 pbw

The diagram below illustrates how the titanate cross-links the system and increases adhesion to the substrate.



Although titanates and zirconates will improve the adhesion to many substrates as they are, plastic substrates require surface modification in order to create reactive functional groups (-OH, -COOH) so that the titanate or zirconate can be fixed to the surface. This modification can be accomplished by corona, flame, or plasma treatments.

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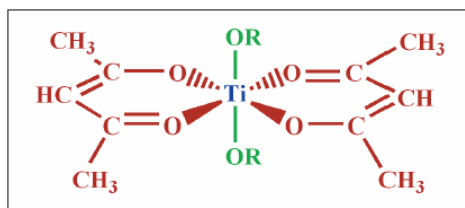
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Tyzor[®] titanates/zirconates for solvent-borne flexographic and gravure printing inks

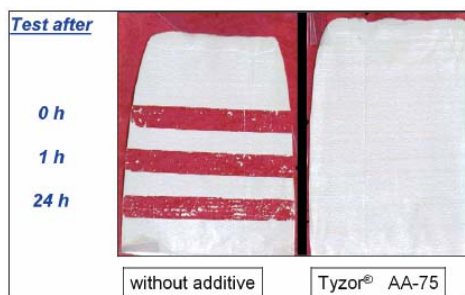
For more than 40 years, Tyzor[®] titanates and zirconates have been used as additives in flexographic and gravure printing inks based on solvent-borne polar functional binder systems, such as nitrocellulose (NC).

Titanium acetylacetonates (AA's) are chelates that are less reactive than traditional alkoxy titanates. Titanium AA's have proven to be very efficient cross-linkers, resulting in improved solvent, water, and heat resistance, substrate adhesion, ink stability, and reactivity during the drying process. The general structure of titanium acetylacetonate is shown below.



The Dorf Ketal line of titanium acetylacetonates includes Tyzor[®] AA, AA-65, AA-75, and AA-105. Differentiation is achieved by varying the alkoxy groups or the solvent content.

The exceptional performance of the Tyzor[®] products is demonstrated in a typical adhesion test (shown below). In the test, most of the ink is removed by adhesive tape from the corona pretreated PP foil sample coated with an ink containing no additives. When 2% Tyzor[®] AA-75 is added to the ink, no delamination occurs, as shown by the sample on the right.



Considerations

When using titanium acetylacetonates in printing inks, there are certain issues to be considered:

- **Acetylacetone (2,4-pentanedione) release**

If acetylacetone is released during or after curing, it can migrate through the foil or can be absorbed at the foil's back side during the wind-up process. This may cause odor issues. In certain applications, acetylacetone is under regulatory pressure.

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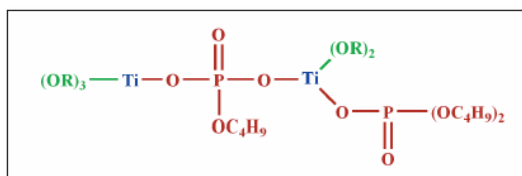
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• **Discoloration**

Titanium acetylacetonates can cause discoloration (yellowing) in some binder systems. Additives such as phenolic antioxidants intensify this effect.

Introducing Dorf Ketal Tyzor[®] IAM

Tyzor[®] IAM is a new grade of titanate specifically developed for the printing ink industry. The structure is shown below.



This new titanium-based phosphate complex helps overcome some of the previously identified performance issues and offers the following features:

- Good stability in solvent-borne printing inks
- Good adhesion promotion and cross-linking properties resulting in improved water, solvent, and heat resistance
- High reactivity during curing
- Low or no discoloration
- No release of acetylacetone
- No known potential for toxic risk
- Effective at low concentrations (1–4%)

Physical/Chemical Properties of Tyzor[®] IAM*

Property	Value
Form	liquid
Color	colorless to light yellow
TiO2 content	ca. 14.7%
Odor	sweet
Pour point	< -50°C
Boiling point	80°C
Flash point	12°C
Specific gravity	ca. 1.0 (25°C)
Viscosity	ca. 20 mPa·s (25°C)
Solubility in water	decomposes in water

* This table gives typical properties. Dorf Ketal does not make any expressed or implied warranty that these products will continue to have these typical properties.

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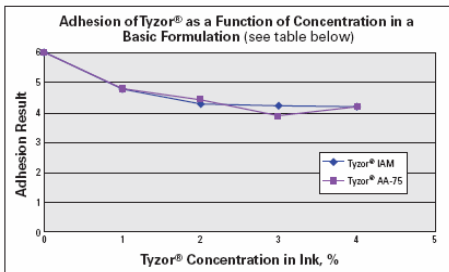
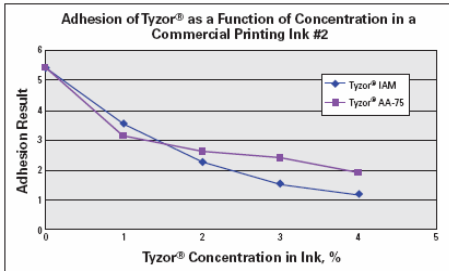
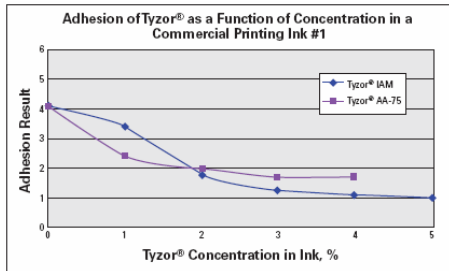
Test Results

Tests substantiate the excellent performance of Tyzor[®] IAM as a printing ink additive. The product was tested in several commercially available printing inks and basic formulations. As shown in the following charts, Tyzor[®] IAM exhibits excellent adhesion and cross-linking performance as well as low discoloration.

Test #1. Adhesion of printing ink to OPP foil as a function of titanate concentration

Procedure: Tyzor[®] IAM or Tyzor[®] AA-75 was added in different amounts to a commercial NC printing ink. The inks were applied and dried at room temperature. Adhesion was measured after 1, 3, 5, 10, 30 minutes, and after 1, 3, 5, 24 hours using adhesive tape pull off.

Results: The results are ranked on a scale of 1 to 6, with 1 representing very good adhesion (no delamination) and 6 corresponding to very poor adhesion (full delamination). The following charts compare the adhesion of the ink containing Tyzor[®] IAM vs. ink containing Tyzor[®] AA-75. In the first two charts, Tyzor[®] IAM shows better adhesion at higher concentration (> 2%) compared with Tyzor[®] AA-75. The third chart shows that the adhesion performance of Tyzor[®] IAM and Tyzor[®] AA-75 in a basic formulation were similar.



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A Basic Formulation Contains:	
Ethanol	32.4 pbw
Ethylacetate	10.0 pbw
Plasticizer	5.6 pbw
Pigment (TiO ₂)	40.0 pbw
NC Resin (35% a.i.)	12.0 pbw
Total	100 pbw

Test #2 Solvent/Water Resistance

Procedure: Tyzor[®] IAM and Tyzor[®] AA-75 were added in different amounts to a commercial NC printing ink. The ink was applied and dried at room temperature. Solvent resistance was measured by applying various 50/50 and 70/30 ethanol/water solutions to the ink for 1 min.

Results: The results showed no significant difference between Tyzor[®] IAM and Tyzor[®] AA-75 in solvent or water resistance. Tyzor[®] IAM consistently produces very good results.

Test #3 Discoloration

Procedure: In a basic white ink, discoloration was measured using a BYK spectrophotometer, using the unmodified ink as a reference. The b-value is an indication of yellowing (higher Δb value indicates stronger yellowing).

Results: As shown in the following table, Tyzor[®] IAM does not produce significant yellowing, even at higher concentrations, when compared with Tyzor[®] AA-75.

Tyzor[®]	Δb (65°)
2% AA-75	0.44
1% IAM	0.01
2% IAM	0.14
3% IAM	0.10
4% IAM	0.15