TYTAN Titanates

RTV Sealents

Industrial Coating

Oilfield Chemicals

Deco Paints

Making a world of difference to Coatings

BORICA


TYTAN - Innovative solutions for a changing world.

Delighting industrial users across the spectrum


Borica is the World’s leading manufacturer of organic titanates and zirconates, which it markets worldwide under the Trade name, TYTAN™.

This useful family of compounds has become so important that in certain areas they are virtually indispensable. They owe their success to their versatility acting as adhesion promoters, catalysts, crosslinkers and surface modifiers.

Creating competitive advantage for you

Our business is highly customer focused. We have aligned our resources and capabilities so that we are best placed to serve our customers. Everything we do is driven by a commitment to increase competitive advantage of our Customers. Where you are targeting a particular market opportunity, we will work in close partnership to develop our TYTAN product as an element of the solution and tailor our technical service to your needs.

Our investment in Research and Development means we are constantly striving to develop our products, ensuring our customers have leading technology at their disposal

...enabling leading paint makers to provide the finishing touch

Borica is the industry leader in titanium and zirconium based thixotropic agents, supplying the world's leading coatings producers.

TYTAN CX decorative coatings range enable them to meet a wide variety of market requirements. They are simple to use in the manufacturing process, needing no specialized equipment.

...proven over 10 years of product development

Our TYTAN products cover a wide range of products for Industrial Coatings. Applications in the industrial sector include Silicone Sealants, Oil Drilling Additives, Heat and Corrosion Resistant Paints, Coupling Agents, Glass Coatings, Wire Enamels and Waterproofing.

Industrial coatings

The Borica products for the industrial coatings market target a wide variety of specific applications, the common factor being the ability to impart enhanced performance. They include curing agents for silicone sealants, coatings to protect the surface of glass, compounds to increase heat and corrosion resistance, to improve fabric waterproofing and to toughen polyester wire enamels.

Product Name	Identification	Suitability	Benefits
TYTAN™ ET	Tetra Ethyl Titanate CAS: 3087-36-3 EC: 221-410-8	• Resin modifier • Sol-gel coatings	• High Ti-content and reactivity • Ambient temperature curing • Improved corrosion resistance
TYTAN™ TNBZ	Tetra n-Butyl Zirconate CAS: 1071-76-7 EC: 213-995-3	• Resin modi-er • Sol-gel coatings	• High Zr-content and reactivity • Ambient temperature curing • Improved corrosion resistance
TYTAN™ TNPZ	Tetra n-Propyl Zirconate CAS: 23519-77-9 EC: 245-711-9	• Resin modi-er • Sol-gel coatings	• High Zr-content and reactivity • Ambient temperature curing • Improved corrosion resistance
TYTAN™ AQZ30	Triethanolamine Zirconate CAS: 101033-44-7 EC: 309-811-7	• Solvent and water based cross-linker • Resin modi-er	• Dual phase exibility • Very strong ionic bonding to metallic substrates
TYTAN™ S6	Di-iso-Butoxy Titanium Chelate (Ethylacetoacetate Titanate) CAS: 83877-91-2 EC: 281-161-1	• Silicone or 2K coatings • Glass coatings	• Improved corrosion resistance
TYTAN™ TIPT	Tetra iso-Propyl Titanate CAS: 546-68-9 EC: 208-909-6	• Silicone or 2K coatings • Glass coatings • Air dry coatings • Sol-gel coatings	• High Ti-content and reactivity • Ambient temperature curing • Improved corrosion resistance
TYTAN™ TNBT	Tetra n-Butyl Titanate CAS: 5593-70-4 EC: 227-006-8	• Silicone or 2K coatings • Glass coatings • Air dry coatings	• High Ti-content and reactivity • Ambient temperature curing • Improved corrosion resistance
TYTAN™ EHT	Tetra 2-Ethylhexyl Titanate CAS: 1070-10-6 EC: 213-969-1	• Silicone or 2K coatings • Glass coatings • Air dry coatings	• Ambient temperature curing • Improved corrosion resistance
TYTAN™ TAA	Titanium Acetylacetonate CAS: 17927-72-9 EC: 241-866-1	• Resin modi-er • Cross-linker • Glass coatings	• High reactivity • Strong adhesion to dicult surface • Improved coupling eect
TYTAN™ X85	Titanium Acetylacetonate CAS: 94233-27-9 EC: 304-059-6	• Resin modi-er • Cross-linker	• Improved corrosion resistance • Improved coating uniformity • Improved adhesion/coupling
TYTAN™ PBT	Polybutyl Titanate CAS: 162303-51-7 EC: 500-687-1	• Air dry coatings • Heat resistant paint	• Very high Ti-content • High performance binder
TYTAN™ TET	Triethanolamine Titanate CAS: 36673-16-2 EC: 253-153-2	• Solvent and water based cross-linker • Resin modi-er	• Dual phase exibility • Very strong ionic bonding to metallic substrates
TYTAN™ AQ33	Aqueous Titanium Chelate CAS: 65104-06-5 EC: 265-409-0	• Wash primer with pH between 6.5 and 8.5	• Improved adhesion and coupling • Improved cross-linking • Environmentally friendly

Further technical information available on request.

Silicone sealants

Neutral cure room temperature vulcanising (RTV) silicone sealants cure at room temperature by the action of atmospheric moisture to form crosslinked, rubbery compounds. They are widely used in the building and construction, automotive, aerospace and electronics industries.

The sealants consist of a reactive hydroxy terminated polydimethyl siloxane liquid polymer, a moisture sensitive silane curing/cross linking agent and a variety of fillers, plasticizers etc. Neutral cure RTV sealants are formulated using alkoxysilanes, which release alcohol, oximino silanes which release an oxime or alkyl and arylamido silanes which release amides on curing. Neutral cure RTV sealants have several problems associated with their use. These include:

- Poor adhesion to some substrates
- Unacceptably long or short cure times
- Poor self-life of the uncured sealant
- Production of cured sealants with unacceptably high modulus.

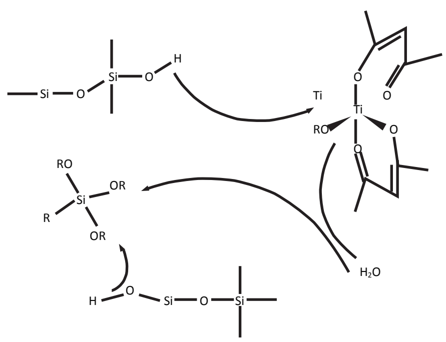
Many of these shortcomings can be overcome using organotitanates such as TYTAN S2. The role of the titanate in these systems is not fully understood but is probably a combination of cross linking, catalytic (hydrolysis of the methoxy terminated curing agent), adhesion promotion, water scavenging and modulus modifying effects. The effects observed depend on the choice of hydroxy terminated polydimethyl siloxane, silane cross linker, filler and plasticizer used. Factors which must be considered, when formulating a sealant, include:

- Viscosity, skin over and tack-free times of the uncured sealant
- Hardness, tensile strength, elongation, modulus and tear and peel strengths of the cured sealant
- The required application properties of the sealant; application temperature, durability, adhesion, compatibility with substrates, compressibility and solvent resistance.

Product Name	Identification	Suitability	Benefits
TYTAN™ TNBT	Tetra n-Butyl Titanate CAS: 5593-70-4 EC: 227-006-8	• RTV sealants • Resin modi-er	• High performance catalyst • Non-toxic catalyst
TYTAN™ TTBT	Tetra t-Butyl Titanate CAS: 3087-39-6 EC: 221-412-9	• Silicone resin	• High reactivity • Reduced yellowing
TYTAN™ S2	Di-iso-Propoxyl Titanium Chelate (Ethylacetoacetate Titanate) CAS: 27858-32-8 EC: 248-697-2	• RTV silicone sealants • Catalyzes hydrolysis of Si-O-Me and cross-links Si-OH groups	• Improved build-up of physical properties • Enhanced adhesion
TYTAN™ S3	Formulated S2	• RTV silicone sealants • Catalyzes hydrolysis of Si-O-Me and cross-links Si-OH groups	• Improved build-up of physical properties • Enhanced adhesion
TYTAN™ S6	Di-iso-Butoxyl Titanium Chelate (Ethylacetoacetate Titanate) CAS: 83877-91-2 EC: 281-161-6	• RTV silicone sealants • Catalyzes hydrolysis of Si-O-Me and cross-links Si-OH groups	• Improved build-up of physical properties • Enhanced adhesion • Extended shelf-life • Liquid at room temperature

The mechanism proposed for the catalysis of hydrolysis of Si-OMe groups by TYTAN S2 is as shown below:

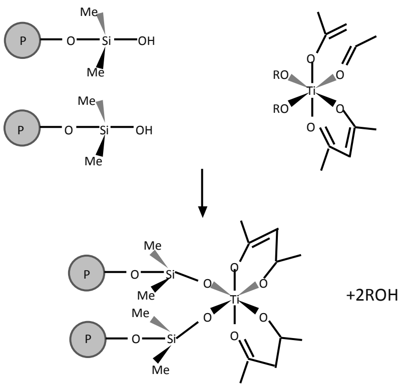
Catalysis of hydrolysis of Si-OMe groups by TYTAN S2



TYTAN S2 catalyses hydrolysis of Si-OMe groups to accelerate cure.

The figure below shows the cross linking mechanism for TYTAN S2 in RTV sealants:

Cross linking mechanism for TYTAN S2 in RTV Sealants



TYTAN S2 can also cross link the silicone to the substrate to give improved adhesion.

Oilfield applications

Metal cross linkers are used to modify the rheological properties of polymer solutions in a wide range of applications. An important example of this use is in hydraulic fracturing (fraccing) where the ability to cross link hydroxl and carboxyl groups in water-soluble polymers is exploited. Delayed and reversible cross linking is often a requirement in this application.

The delayed cross linking allows low viscosity fluid to be pumped to the formation before the viscosity rises to, for example, support the propant and produce satisfactory subterranean fractures. Fracturing fluids are commonly based on polysaccharides such as guar gum, locust bean gum, hydroxyethylcellulose and modifications of these polymers.

TYTAN Zirconates/Titanates act as cross-linking agents for guar derivatives. They provide hydraulic fracturing fluids with excellent capabilities of propagating the fracture by transmitting hydraulic pressure to the formation and transporting the proppant into the created fracture.

Product Name	Identification	Suitability	Benefits
TYTAN™TNBZ	Tetra n-Butyl Zirconate CAS: 1071-76-7 EC: 213-995-3	• Raw material for organo zirconate cross-linker	• High reactivity
TYTAN™TNPZ	Tetra n-Propyl Zirconate CAS: 23519-77-9 EC: 245-711-9	• Raw material for organo zirconate cross-linker	• High reactivity
TYTAN™ AQZ30	Triethanolamine Zirconate CAS: 101033-44-7 EC: 309-811-7	• Fracturing fluid	• High temperature stability • Wide pH range
TYTAN™ AQZ40	Alkanolamine Zirconate CAS: 141760-22-7	• Fracturing fluid	• High temperature stability • Wide pH range
TYTAN™ AQ33	Aqueous Titanium Chelate CAS: 65104-06-5 EC: 265-409-0	• Fracturing fluid	• High reactivity • Chelated cross-linker • Low cost
TYTAN™ TAA	Titanium Acetylacetonate CAS: 17927-72-9 EC: 241-866-1	• Fracturing fluid	• Chelated cross-linker • Low cost
TYTAN™ TET	Triethanolamine Titanate CAS: 36673-16-2 EC: 253-153-2	• Fracturing fluid	• Dual phase flexibility • Chelated cross-linker • Low cost

Heat and corrosion resistant paints

This is one of the earliest uses for organic titanates. The formulation of heat-resistant coatings based on organic titanium derivatives, particularly butyl titanate, was first described by Winter et al.[4] in 1947. Since that time several developments have occurred, including the use of polymeric butyl titanate, and the discovery that alkyl titanates can be used to modify heat-resistant paints based on silicone resins to make them airdrying.

When used in conjunction with leafing aluminium and other metal pigments, butyl titanate, either monomer or polymer, gives paints that remain resistant at temperatures up to 600°C. The formulation of a typical paint is:

	Wt.%
Leafing aluminium pigment (65% dispersion)	36
TYTAN PBT (20% Ti)	32
Ethylcellulose (10% solution)	5
Aromatic white spirit	27

The use of zinc-rich primers has been suggested, but these coatings have an upper temperature limit of about 400°C. The following formulation has been found satisfactory:

	Wt.%
Zinc dust	62
TYTAN PBT (20% Ti)	21
Ethylcellulose (10% solution)	2
Aromatic white spirit	15

No special technique is required to make these paints. The pigment is dispersed in a portion of the solvent with the ethylcellulose added, and the titanium compound is stirred in last. The titanate may be added as a solution in aromatic or ordinary white spirit if desired. The paint may be applied by brush, but spray application is preferable.

One serious disadvantage of the otherwise excellent paints based on silicone resins is the necessity to bake the finish in order to cure it. It has been found that incorporating an organic titanate into silicone-based paints enables them to be cured after a short time at room temperature. Most silicone resins recommended for use in heat-resistant paints respond to this treatment.

Suitable titanium compounds are iso-propyl, butyl and polybutyl titanates, the first being preferred. A recommended formulation is as follows:

	Wt.%
Silicone resin	34
TYTAN TIPT	10
Leafing aluminium pigment (65% dispersion)	26
Solvent (eg aromatic white spirit)	30

It is strongly recommended that these paints be applied by spraying. If brush application is unavoidable then polybutyl titanate should be used and the solvent proportion reduced to half. Because these heat-resistant paints contain organic titanates, they should be protected from unnecessary exposure to moisture during manufacture and storage.

In titanate-cured silicone resin paints the film dries by the formation of Ti-O-Si links, and it remains resistant to thermal decomposition at above 400°C. Paints based wholly on titanates dry because the titanate film is progressively hydrolysed to a thin layer of polymeric titanium oxide, and this serves to bond the pigment flakes together and to the substrate. After service at high temperatures all the organic residues are removed, and the remaining film is totally inorganic. These paints are useful up to 600°C.

Surface preparation is very important, and a completely rust-free surface required, preferably shot-blasted, if adequate adhesion is to be obtained.

Coloured paints can be formulated with suitable coloured pigments that withstand high temperatures without alteration in colour or decomposition. Because of the porous nature of films formed with such pigments, these paints must be applied over a non-porouspriming coat containing leafing aluminium pigment, otherwise the substrate corrodes through oxidation at high temperatures.

Glass-coating (titanizing)

One of the more unusual, though extremely useful, applications organic titanates is in the coating of glass and ceramic surfaces with an extremely thin layer of titanium dioxide, produced by pyrolysing the organic titanium compound on the hot surface of the article to be coated.

This layer is usually about 50nm thick, and invisible, although it can impart brilliance or lustre to the article. These thin films are particularly hard, and impart a high degree of scratch resistance to glass surfaces by reducing the coefficient of friction.

Effective scuff resistant surfaces are most important for bottles and other glass containers used in industries where abrasion on high-speed bottling lines may be severe, and lead to inconvenient and expensive stoppages.

Work carried out has shown that the scuff resistance of glass can be greatly increased by treating the hot glassware with organic compounds of titanium, whereby a thin, transparent film of titanium dioxide is left keyed into the surface.

This process is of much interest to glass manufacturers and users, since it is probable that breakages, both during the later stages of production and during use, can be reduced thereby.

The titanizing process is not restricted to glass bottles. Float glass, plate glass and glass or rock wool fibres can also be strengthened in this way.

The effects of similar treatment upon other glassy substrates (vitreous enamel and glazed pottery) were also likely to be of interest, and further work has been carried out in order to study them.

Organic titanium compounds may be applied to glassware by three different methods

1. Vapour process

The most volatile titanate, TYTAN TIPT is metered into a stream of heated dry air (or nitrogen) and directed onto a heated surface where it vaporizes. The titanate-air mixture then passes into a chamber or tunnel, interposed between the bottle-forming machine and the annealing lehr, where it contacts the glass articles at temperatures of 450-550°C. The best titanate:air ratio for each system is found by experimentation. It is governed by the glass temperature and the rate of movement of bottles through the titanizing chamber. Usually the exhausted vapours from the chamber are recirculated to improve economy.

2. Spraying process

Organic titanium compounds may be applied to glass by spraying, either on the hot ware, when pyrolysis occurs at once, or on the cold ware, which is subsequently heated to pyrolyze the coating. The hot process is preferred where articles are produced at low unit cost (e.g. milk bottles), since production lines may be readily adapted to include the process and no extra heating is required. The cold process may be used to advantage with articles of high unit cost (e.g.television tubes), where the loss from stopping the production line would be more than compensated by fewer rejects and improved quality.

Any liquid organic titanium compound, including polymers such as polybutyl titanate, is suitable for application by spraying. However TYTAN TIPT is the most convenient, since it can be used in a variety of ways.

3. Dipping process

The cold glassware is degreased, immersed in a solution of organic titanium compound, and then allowed to drain. After air-drying, the ware is heated to the annealing temperature (400 °C to 650°C). A wide variety of solutions can be used for the treatment, and a few examples will be mentioned by way of illustration. For instance TYTAN TET has been successfully tested in water alone and a number of solvents including methanol, ethanol and butanol, each with and without added water. TYTAN PBT can be used in solution

in various solvents such as industrial spirit, isopropyl alcohol, and butanol. The use of an organic solvent, though wasteful if not necessary, gives quicker drying.

The dipping process is the least wasteful in terms of amount of titanium compound used, and the thickness of coating can be adjusted by varying the concentration of the solution.

It is considered that the treatment of glass with organic titanium compounds will prolong the useful life of the ware.

Wire Enamels

Due to their polyfunctional nature organic titanium compounds are excellent crosslinking and curing agents for polymers with hydroxyl groups on their chains. Examples of such polymers are cellulose derivatives, polyvinyl alcohols, and polyesters.

An important use of titanium alkoxides in the polyester resin field is for the crosslinking of such resins, both conventional terephthalate polyesters and polyester-amides, used in formulating wire enamels designed to operate at high temperatures. Such enamels are mainly employed on the windings of compact electric motors: the higher the temperature that the windings can withstand, the more economically the motor can be made.

As well as their exceptional heat resistance, such wire enamels have excellent mechanical properties, and are highly resistant to abrasion and solvent attack. It has been stated that the titanium alkoxide sometimes alters the rheological character of the enamel so that flow is improved at the wire coating stage.

The titanium alkoxides commonly used are isopropyl titanate, butyl titanate and butyl titanate polymer. The amount to be used depends on the constitution of the resin, but is generally about 5%. The resin is first dissolved in a solvent, usually a mixture of cresols, and the titanate is added and stirred. The enamel, after coating onto the wire, is heat-cured at about 350°C. Recommended products would include TYTAN TNBT

Since the lower alkoxides can exchange alkoxy groups for aryloxy groups in the cresol solvent, it is sometimes the practice to use a cresyl or polycresyl titanate as a crosslinking agent.

Wire enamels for the windings of compact electric motors and other heavy duty users must be capable of withstanding extremes of mechanical, electrical and thermal stresses. In addition they need to adhere to wire, have the correct flow properties during application and must cure quickly at a reasonable temperature. The benefits over other types of catalysts and crosslinking agents are:

- Increased cure rates
- Lower cure temperatures

Decorative Coating

Todays, home decorators take a professional finish for granted. They can load the brush or roller with emulsion paint and there are no drips. The paint flows on to the surface without spatter. A single application is all that is needed to leave a thick even finish with no brush marks or sagging. Such results have only been achievable in water based gloss, silk and matt paints for the home improvement market since the development of structuring agents made by Borica.

Structured paints have a pleasing gel-like consistency in the can. Being thixotropic, the paint breaks down under the shear force of application by brush or roller. After application the structure builds up again to prevent sag. There is sufficient time delay before restructuring to allow levelling of brush marks to take place as in non-structured paint.

Building upon innovation

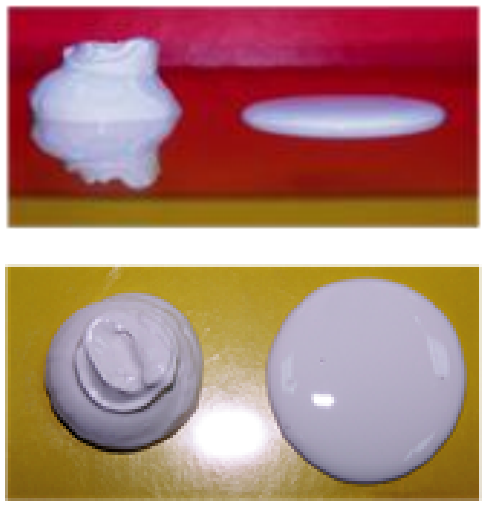
The coatings team at Borica has inherited the knowledge of the innovators who first used titanium compounds as structuring agents, thus bringing about the dawn of non-drip paints in the 1960's. We have built upon this legacy to meet the needs of paint manufacturers in an ever changing market with four decorative coatings products.

Applications range from highly structured paints using TYTAN CX100 to paints for low VOC environments containing TYTAN CX400. This product enables you to comply with VOC related regulations for both environmental and health hazards and satisfy any consumer concerns about VOCs in the paint itself. In today's quality and safety conscious market it sets the standard.

Product Name	Identification	Suitability	Benefits
TYTAN™ CX100	Alkanolamine Titanate CAS: 68784-47-4 EC: 272-249-5	• Water based decorative paints • Colloid stabilized Gloss, Silk and Matt	• Rapid structuring • Broad binder system compatibility • No reformulation cost
TYTAN™ CX200	Alkanolamine Titanate CAS: 68784-48-5 EC: 272-250-0	• Water based decorative paints • Colloid stabilized Gloss, Silk and Matt	• High level structure development • Enhanced shear resistance • Easier controllable processing • No reformulation cost
TYTAN™ CX300	Alkanolamine Titanate EC: 405-250-8	• Water based decorative paints • Colloid stabilized Gloss, Silk and Matt	• Delayed structuring • Reduction of production costs through very easy processing
TYTAN™ CX400	Alkanolamine Titanate CAS: 1072830-14-8 EC: 410-660-5	• Low VOC • Water based decorative paints • Colloid stabilized Gloss, Silk and Matt	• Zero contribution to VOC of finished paint • Delayed structuring • Reduction of production costs through very easy processing
TYTAN™ ZPN	Ammonia Zirconium Lactate CAS: 68909-34-2 EC: 272-702-7	• Low VOC • Water based decorative paints • Surfactant stabilized Gloss, Silk and Matt	• Zero contribution to VOC • Very cost effective

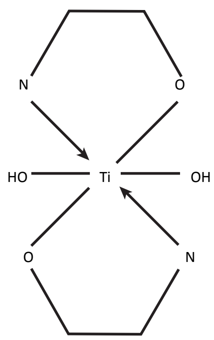
How TYTAN structuring agents work

When added to water based paints the titanium compound reacts with the water to give an active species. This in turn cross links with the polymer binder in the paint, producing the rheology modifications which give the paint its thixotropic structure. Titanium alkoxides are rapidly hydrolysed by water in a reaction that proceeds via intermediate hydroxy compounds which decompose to produce titanium dioxide. The TYTAN CX range is made up of titanium alkoxides which have been rendered water soluble and stable to hydrolysis by reacting them with certain chelating agents. The original titanium chelate used in structuring paints, TYTAN TET, is believed to form a stable intermediate which is typical of the range, as shown below.



Increasing CX product addition increases the gel strength of th e paint.

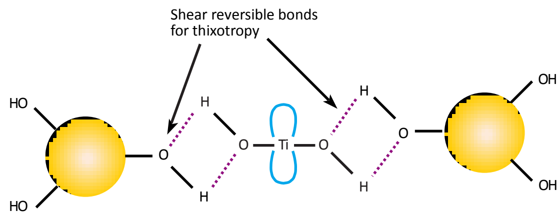
Partially hydrolysed TYTAN TET



The reaction

The TYTAN CX products were developed for use in conjunction with, and not as an alternative to, emulsion paint thickeners. Hydroxyethyl cellulose (HEC) is incorporated into colloid stabilized binders during their manufacture and forms hydroxyl and carboxyl groups on the surface of the polymer particles. It is believed that physical cross linking occurs as hydroxyl groups on the partially hydrolyzed titanate interact by hydrogen bonding to the functional groups on the polymer particles shown below.

Formation of shearable bonds for thixotropy



The result

The energy of the hydrogen bonds is such that the structure breaks down when the paint is applied by brush or roller allowing it to flow. When the shearing force is removed, the structure slowly reforms i.e. thixotropic rheology is observed. The delay in recovery of structure is slow enough to allow flow and levelling, yet quick enough to prevent sag.

The simplicity

The use of TYTAN CX products in conjunction with conventional cellulosic or with associative thickeners can considerably simplify formulation to achieve a better balance of paint application properties.

They are liquid products designed to be added to the finished paint so you can achieve a range of structures without needing to reformulate. Although there can be interaction between titanates and cellulose ethers used as paint thickeners, this is generally weak compared to that between the titanate and a colloid stabilized binder. This has been demonstrated by comparing the reactivity of TYTAN CX200 and TYTAN CX300 in paints made with colloid and surfactant stabilized binders and a range of HEC thickener addition levels.

The use of TYTAN CX products in paint manufacture

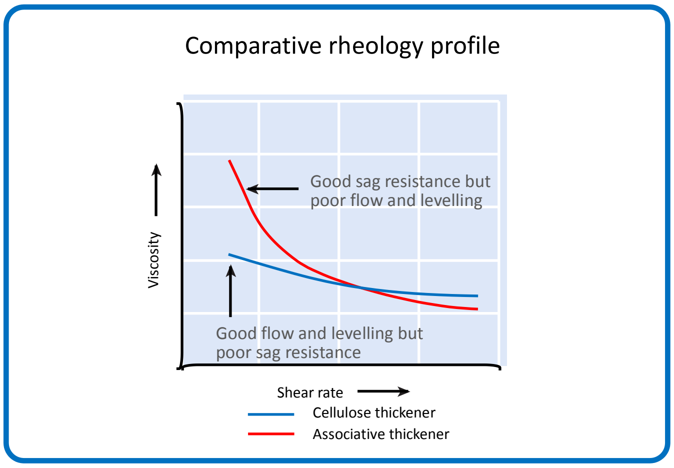
The use of the TYTAN CX range of structuring agents in emulsion paints is very simple. Amongst the many components that may be used to make the paint, the only one which affects the structure in conjunction with the additive is the paint binder. This ease of use gives the manufacturer more flexibility than other structuring agents. No special equipment is required, the additive being mixed in at the last stage of manufacture. The different degrees of shear stability within the TYTAN CX range affect how this process should be carried out.

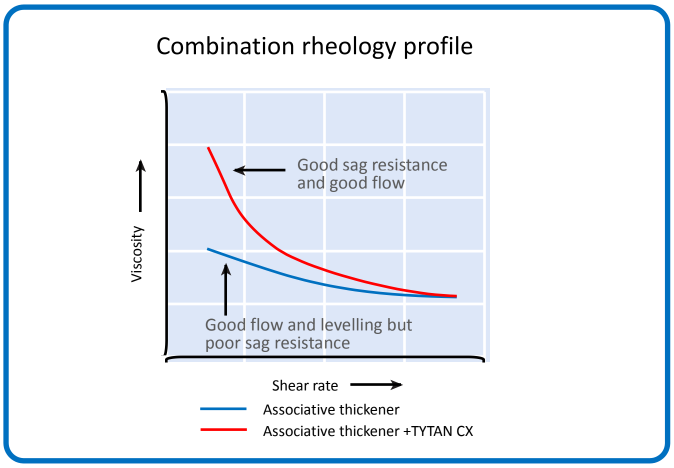
The role of paint thickeners

Paint properties such as gloss, brush drag, film build, levelling, spatter and sag resistance are all affected by the selection of the paint thickener to be used in conjunction with TYTAN CX products.

Cellulose based materials such as hydroxyethyl cellulose and sodium carboxymethyl cellulose and (to a lesser extent) certain polyacrylates have dominated the emulsion paint thickener market and are still commonly used. However, a new class of thickeners, associative thickeners, are now bringing paint manufacturers additional advantages.

These low molecular weight synthetic polymers or modified cellulosics are stable to enzymatic degradation and impart a more Newtonian rheology (see figure below). Higher viscosity at high shear, giving good brush drag and film build, is combined with lower viscosity at low shear to give good flow and levelling. The latter, however, may also lead to poor sag resistance and pigment settling. The use of TYTAN CX products in conjunction with associative thickeners increases the low shear viscosity, thus improving sag resistance and anti-settling properties.





The use of TYTAN CX products in conjunction with associative thickeners increases the low shear viscosity, thus improving sag resistance and anti-settling properties.

TYTAN products may also complement the anti-spatter properties of associative thickeners and improve the paint's in-can appearance. Because the recovery of low shear viscosity after application is delayed for paints structured with TYTAN compounds, they do not detract from the good flow and levelling properties imparted by associative thickeners.

Paints based on cellulose thickeners exhibit marked pseudoplastic rheology, giving relatively low viscosity at high shear and relatively high viscosity at low shear. Thus the paints often exhibit good sag resistance but poor flow and levelling properties. Partly replacing a cellulose thickener by a TYTAN CX product in an emulsion paint formulation can improve flow and levelling properties whilst maintaining, or even improving, sag resistance. Spatter resistance can also be improved.

The partial replacement of a cellulose thickener with a TYTAN organotitanate has the added advantage of removing some of the biodegradable and water soluble material from the dried paint film. This may improve weatherability and washability. As a general guide no more than half of the cellulose thickener should be replaced or the paint may be unstable.

The effects of other formulation parameters

pH

Unlike some other metal organic complexes, it is not necessary to adjust pH in order to obtain structure when using TYTAN titanates. We recommend that the paint is made at the pH required by other components and that the structure is controlled by choice and quantity of titanate. Variations in the structure of the paint are not likely to occur if the pH of the finished paint changes on storage.

Tinters, surfactants and glycols

TYTAN titanates can be used to structure coloured paints. Heavy tints may require a greater quantity than white or pastel shades, because large amounts of the surfactants usually present in tinters can reduce the TYTAN products' efficiency.

TYTAN CX compounds do not affect the colour of tinted paints. The TYTAN thixotrope, should be added in the factory after tinting operations have been completed.

Nevertheless, in-store tinting can be carried out with factory-structured paints. In commercial production of such paints, formulations should be developed bearing in mind that more titanate may be required for heavy tint bases. The mixing required in-store will temporarily break down the structure, but this should re-form within a few hours. The rate and degree of gel recovery should be checked on the proposed formulation before such a system is marketed.

Certain glycols commonly used as wet-edge stabilizers in glossy emulsion paints may inhibit gel formulation when present in concentrations of around 10%. This effect can be successfully counteracted by increasing the concentration of the TYTAN titanate or by using one of the more reactive compounds from the TYTAN CX series. Although surfactants, when used in large quantities, may inhibit the reactivity of TYTAN CX compounds, it is imperative to use sufficient surfactant to disperse pigments and extenders adequately. Generally, considerably more than the minimum amount of dispersant needed for adequate dispersion can be used without impairing the structure imparted by titanates.

Pigments and extenders

Although they can impart structure to a paint in their own right, we are not aware of any systems in which pigments and extenders affect the additional thixotropic structure imparted by TYTAN products.

Syneresis

In practice it has been found that using TYTAN structuring agents neither promotes nor aggravates syneresis, but this phenomenon is more noticeable in highly structured paints than in paints with lighter structures. If syneresis is a problem other formulation parameters should be examined.

Some remedial steps include using extenders with a Higher water demand, replacing some or all of a colloid thickener with one of a higher molecular weight or adding an anionic thickener.

Shear stability with titanates

For reasons of shear stability, the TYTAN range of structuring agents should be added at the last stage of manufacture and the paint should then be canned off with minimum delay. If a two-speed stirrer is available then the titanate should be mixed into the paint at the faster stirring rate to aid incorporation. Thereafter stirring should be slow.

Maintaining stability

Shear applied to paint containing a TYTAN structuring agent will temporarily break down the structure. Although this structure slowly reforms when the shearing force is removed, it does not recover fully. A small number of the hydroxyl groups on the partially hydrolysed titanate may react with each other or with other components of the paint, an effect generally only significant when excessive shear is applied. Some degree of shear is obviously unavoidable when a paint is canned off, but if the shear applied to each batch of paint is similar and canning-off time is reasonably constant this is not a problem.

Permanent loss of some structure due to shear will occur only after the titanate has begun to undergo hydrolysis in the water based paint. Because the more reactive titanates, such as TYTAN CX100, structure more rapidly, they are more affected by shear applied soon after adding the titanate to the paint. As any consequent loss of structure is more noticeable for TYTAN CX100 than TYTAN CX200, the latter is termed more shear stable. If there is considerable variation in the shear applied after the titanate has begun to react, this may also cause the paint's final gel strength to vary, an effect more noticeable for the more reactive titanates. If difficulties are likely in maintaining reasonably constant shear and canning off times from batch to batch and a reasonably reactive titanate is needed, we recommend TYTAN CX300 for optimum consistency.

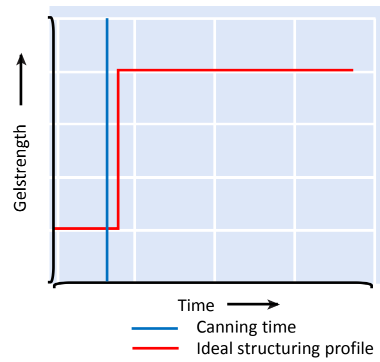
The titanates are generally more sensitive to shear at high temperatures. Even when the applied shear is constant from batch to batch, variations in temperature at the point of titanate addition may also cause variations in the final gel strength. This effect varies depending upon the particular paint formulation and type and quantity of titanate added.

TYTAN CX300 was developed as a 'shear stable' alternative to TYTAN CX200 to reduce any inconsistencies in structure caused by variable shear which only occurs once the titanate has started to react with water and other paint components. Ideally, the titanate would not begin to react until the paint was canned off (as represented below), bringing two advantages:

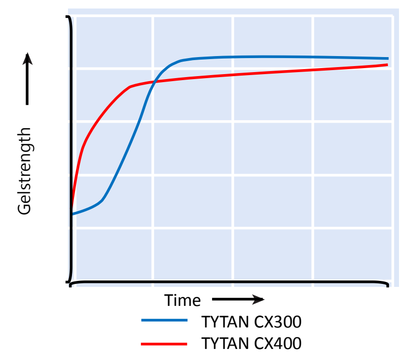
- less titanate would be required to afford the same structure, and
- inconsistencies in production methods would not result in inconsistencies of the titanate's effectiveness.

Typical reactivity profiles of TYTAN CX200 and TYTAN CX300 are compared in the following figure:
TYTAN CX400 is the most recent addition to the range of products. It was developed as a 'shear stable' structuring agent for solvent free formulations. TYTAN CX400 has the same shape reactivity profile as TYTAN CX300. However, because of the lower titanium content of TYTAN CX400, a higher addition level is required to afford the same degree of structure.

Ideal reaction profile



Reactivity profiles of TYTAN CX products



TYTAN CX400 was developed as a ‘shear stable’ thixotrope for VOC free applications

Testing the suitability of TYTAN CX products

Rheology measurements for gel strength

These properties are also related to paint spread, film thickness and hence covering power. Gel strength is a measure of the degree of structure in a paint, and it is related to its appearance in the can.

Commercially available instruments for the measurement of gel strength and viscosity include:

The Stevens texture analyser: Operated by forcing a plunger a fixed distance into the paint test sample, it measures the force required to achieve this penetration.

The ICI gel tester: This commonly used alternative measures the force required for a slowly rotating paddle to break down the structure of a paint. There is an approximately linear relationship between the results obtained on these two instruments.

Paints testing formulation

Paints were prepared according to the following formulation:

For the first paint a colloid stabilized binder was used, the second used a surfactant stabilized binder.

In each case the concentration of the HEC solution was varied to produce paints with HEC contents of 0.10 and 0.2%.

100g samples of each paint were dosed with TYTAN CX200 or TYTAN CX300 at 0.1% and 0.5% addition. The gel strengths of the samples, along with those of control samples with no titanate added, were measured after 24 hours using a Stevens LFRA Texture Analyser.

The Texture Analyser was fitted with a 25mm cylindrical probe and machine settings of 10mm probe depth and 2mms-1 probe speed were used.

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Test results

The 24 hour gel strengths measured for the paints containing the two types of binder are shown in the following graphs. The first graph shows the results achieved for TYTAN CX200. The degree of structure achieved with the surfactant stabilized binder is low compared to that achieved with the colloid stabilized binder and that the addition level of HEC has no significant effect on the structure. The second graph, for TYTAN CX300, shows the same behaviour.

	Parts by weight
Water	160.0
'Calgon S' (5% solution)	44.5
'Rhodasurf 1' (10% solution)	12.2
Butyl cellosolve acetate	12.2
Biocide	0.8
'Natrosol 250MR' HEC (3% solution)	63.4
TiO2	231.9
Calcined china clay	25.2
Ground calcite	97.9
Binder	351.1
0.880 Ammonia	0.8
Total	**1000.0**

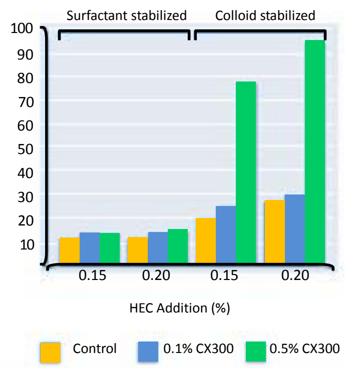
The results of this experiment confirmed that structuring due to interaction of the titanate with added HEC thickener is very low compared to the effect of the titanate-colloid stabilized binder interaction.

TYTAN CX products are not recommended for use with binders stabilized with polyvinylalcohol as irreversible gelation tends to occur

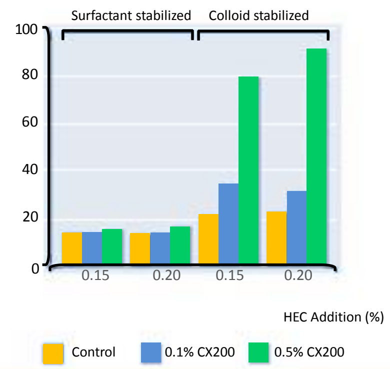
Choice of binder

The type of binder stabilization used is not always evident from the manufacturer's literature. Even when a binder is known to be colloid stabilized, its degree of reactivity with titanates cannot be predicted. The method of manufacture of commercially available colloid stabilized binders, and hence their reactivity towards titanates, varies considerably. The suitability of a binder for use with organotitanates can only be determined experimentally. About 1% of TYTAN CX100 should be mixed into a finished paint containing the binder to be tested. A shear-reversible structure which begins to form within one hour indicates that the binder is suitable for use with titanates. The degree of structure can be increased or decreased by altering the type or quantity of titanate added. As a rough guide, between 0.1% and 1.0% by weight on finished paint of a TYTAN CX is normally required although in a very highly structured paint more than 1% may be used. An alternative, but less reliable, test to determine the suitability of the binder is to add 1-2% by weight of TYTAN CX100 directly to the binder (preferably diluted 50:50 with water). If a shear-reversible structure begins to form within a few minutes, then the binder should be suitable for use with TYTAN CX products. If the binder does not thicken noticeably within one hour, it is probably unsuitable for use with titanates. This should, however, be regarded as a quick screening test; it is recommended that a finished paint, rather than the binder alone, is tested.

The effect of binder type and HEC addition level on gel strength with TYTAN CX300



The effect of binder type and HEC addition level on gel strength with TYTAN CX200



The TYTAN advantage

For industrial and decorative coatings

- The world-leading TYTAN range of advanced structuring agents for decorative water-based gloss, silk and matt emulsion paints.
- Excellent gloss, flow and anti-spatter properties to emulsion paints.
- TYTAN range of industrial coatings products for use in a variety of applications such as: silicone sealants, corrosion and heat resistant paints, wood coatings, wire enamel, glass coating and waterproofing.
- Proven over 10 years of product development.
- Unique understanding of customers needs through working in partnerships.
- Product supply and technical service tailored to individual customer needs.
- The ability to focus the relevant resources of the whole Borica group on achieving your goals.
- Applications teams specialising in meeting the needs of both decorative and industrial coatings manufacturing customers.
- World-wide sales support network, providing before and aftersales support.

How to find out more

If you would like further details about working with Borica, please contact your local representative or office, or alternatively look at our website.

We will be pleased to show you how to achieve the optimum solution to your needs by working in partnership with Borica. In addition, we will of course provide you with any further literature about Borica and technical information about our products.
We invite you to get in touch today.
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