

Titanium-Hydrogen Peroxide Compounds

D. G. Nicholson

University of Illinois, Urbana, Illinois

“After yellowing” of white paints and enamels has been a problem of importance to the paint and pigment manufacturers. Lithopone paints have a tendency to yellow when exposed to darkness (behind pictures, mirrors, etc.), while titanium dioxide whites have a tendency to yellow when exposed to light.

The yellowing of the titanium dioxide paints is explained by the fact that peroxide linkages formed at the unsaturated bonds in the vehicle during the drying process tend to oxidize some of the titanium dioxide to pertitanate, in which form the titanium is present in a valence form higher than four.

A study conducted using anhydrous ethyl acetate as the solvent with titanium tetrachloride and anhydrous hydrogen peroxide as solutes has shown that an addition product is formed between the two compounds. This addition compound is insoluble in the ethyl acetate solution. Upon standing at room temperature or upon contact with water the material changes from white to the orange red of pertitanate material. The decomposition is accompanied by liberation of oxygen, hydrogen chloride and water. The water formed in this decomposition evidently serves to cause some dissociation resulting in the orange-red colored surface. The white material is very soluble in water producing the red-orange aqueous solution of pertitanate. The white compound is evidently a coordinated compound containing titanium chloride and hydrogen peroxide.

Since paint films are virtually anhydrous in nature, it follows that the yellowing of the titanium dioxide films could be attributed to a peroxide coordination between the peroxide linkages in the vehicle and the titanium dioxide particles in the film, rather than a true oxidation of the titanium dioxide molecule in the semi-solid film. This coordination or yellowing is catalysed by light as well as moisture.

Laboratory tests made using titanium hydroxide and a solution of dry hydrogen peroxide in ethyl acetate show an immediate definite yellowing of the titanium dioxide particles. This same yellowing effect is also observed when air is bubbled through a suspension of titanium hydroxide in turpentine for a period of two weeks or longer.