The Effect of TiO_2 Pigment on the Performance of Paratoluene Sulphonic Acid Catalysed Paint Systems

*Elizabeth Reck, Steve Seymour**

Huntsman Tioxide, Haverton Hill Road, Billingham, TS23 1PS, UK

Summary: The work has highlighted the importance of choosing the correct TiO_2 pigment for paratoluene sulphonic acid (PTSA) catalysed paints. Generally, surface treated TiO_2 grades which are basic in nature resulted in the best optical performance in comparison to acidic surface treated grades. The relative performance of the acidic surface treated grade can be improved by increasing the PTSA level in the paint or by using a resin with a higher acidity level. It is postulated that for these TiO_2 grades, the higher acid levels were found to give better steric repulsion. However, overall, the basic surface treated grade retained the best optical performance in PTSA catalysed paint systems.

Keywords: acid catalysed paints, cure time, resin acidity, TiO_2, optical performance

Introduction

In industrial paints, the choice of TiO_2 generally has little effect on cure rate and degree of cure. However, in paints where cure is catalysed by an acid such as PTSA, the TiO_2 affects the curing mechanism. The effect the TiO_2 has on the cure depends on the pigment coating.

Virtually all commercial TiO_2 pigments are now coated. Originally, the purpose of coating was to improve durability and to lessen yellowing which occurred in certain types of paints. However, it was subsequently found, that surface treatments could be used to improve the dispersibility of pigments in different media.

As the name implies, coating involves the deposition of other matter onto the surface of the pigment particles. The coating agent must be a white, hydrated oxide; silica, zirconia, titania and alumina are commonly used. In the case of silica, it can be used to form several types of coating. It is often used in combination with alumina to form either a loose porous coating or a relatively compact coating. An even denser coating, known as a 'dense silica' coating can be formed to give a highly impermeable layer which has excellent durability. The more silica there is in the coating, generally the more acidic the pigment surface will be, whilst a pigment

 CCC 1022-1360/00/$ 17.50+.50/0

where the presence of alumina and zirconia dominate in the coating will be more basic in nature. Previous papers[1,2,3] have shown how basic TiO_2 pigments can neutralise the PTSA and hence reduce its catalytic effect. If the catalytic effect is reduced, increased paint cure time would be expected.

This paper focuses on the performance of TiO_2 pigments in PTSA catalysed paint systems and how an increased paint cure time can affect the optical paint performance.

The influence of resin acidity on cure and optical performance is also studied. In earlier papers[4,5,6] published by Huntsman Tioxide the effect of the resin acidity on TiO_2 pigments and, ultimately, the optical performance of coating was discussed.

The main finding of these earlier papers was the importance of matching the acid-basic nature of the TiO_2 pigment with the acid-basic nature of the resin. For example, TiO_2 pigment with a predominantly acidic surface offers a lot of potential reaction sites for resins with a basic nature which results in the resin molecules lying flat on the pigment surface. This gives a compact adsorbed layer with little scope for solvent entrapment between the pigment and resin. Such compact resin layers have little steric repulsion, as shown diagrammatically in Figure 1(a), and lead to poor stabilising properties and poor optical paint performance.

This paper examines the use of acid in such systems to enhance the steric repulsion between pigment particles and, hence, improve the stabilising properties. If acid (e.g. in the form of an acid catalyst) is added to a system, the acid should compete with the acidic TiO_2 pigment for the basic sites on the resin molecules resulting in fewer reactions taking place between the resin and the TiO_2 pigment. This should result in a less tightly packed resin layer around the TiO_2 pigment, giving more scope for solvent entrapment between the resin and pigment, leading to better paint stability. See Figure 1(b).

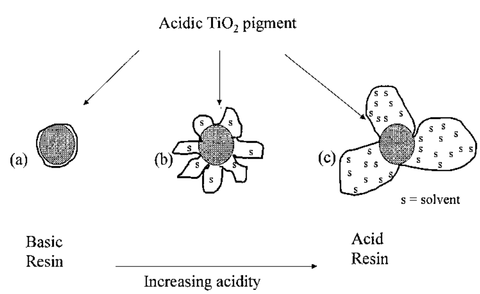

Figure 1. Resin acidity effect on an acidic TiO_2 pigment

Figure 1(c) shows the theoretical situation where so much acid has been added to the paint that the acid significantly reduces the number of basic sites on the resin. Hence the resin is only attached to the TiO_2 pigment to a very small degree leading to significant solvent entrapment. The resin molecules are significantly extended from the pigment surface resulting in excellent steric repulsion and good paint stability.

In a similar manner this paper also examines the use of acid when TiO_2 pigments which are predominantly basic are used.

If a basic resin is used with a basic TiO_2 pigment, there are few opportunities for reaction between the two leaving opportunities for solvent entrapment and extended resin molecules around the TiO_2 pigment. This should again result in excellent steric repulsion and good paint stability as shown in Figure 2(a).

However, if acid is added in increasing amounts to such a system, it will, in theory, react increasingly with the basic resin making it more acidic. This should result in more interaction with the basic TiO_2 pigment leading, ultimately, to poorer steric repulsion. This is illustrated in Figures 2(b) and 2(c).

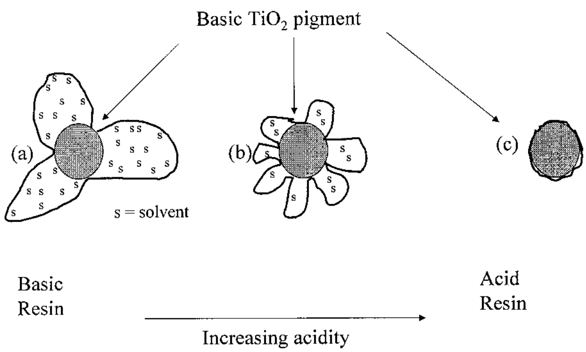

Figure 2. Resin acidity effect on a basic TiO_2 pigment

Part 1 - Effect of TiO_2 on Cure Time and Gloss in a PTSA Catalysed Paint System

To illustrate the effect of TiO_2 grade on cure in a PTSA catalysed system, paints were produced using 12 TiO_2 pigments with different acidic and basic surface treatments as shown in Table 1.

Table 1 – Surface treatments of the twelve evaluated TiO_2 pigments

Pigment name	Pigment coating	Acid-basic nature of surface coating
TR81	Alumina-zirconia	Predominantly basic
TR85	Alumina-zirconia-silica	Some acidity
R-HD2	Alumina	Predominantly basic
R-TC90	Alumina	Predominantly basic
G22/53	Alumina-zirconia-silica	Some acidity
G15/49	Alumina-zirconia	Predominantly basic
TR92	Alumina-zirconia	Predominantly basic
G63/2	Alumina-zirconia-silica	Some acidity
G9/32	Dense silica	Predominantly acidic
G22/62	Dense silica	Predominantly acidic
G9/72	Dense silica	Predominantly acidic
G63/1	Dense silica	Predominantly acidic

The cure time of the paints was determined by monitoring the viscous and elastic behaviour changes on a controlled stress rheometer during paint curing. The results are illustrated in Figure 3 where a wide range of paint cure times can be seen for the twelve pigments ranging from just below 700 seconds up to 870 seconds.

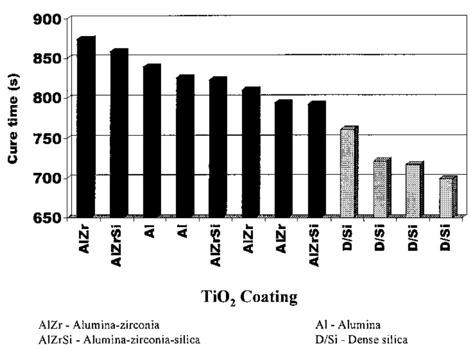

Figure 3. Effect of TiO_2 coating on the cure time of a PTSA catalysed paint system

The four pigments which have the shortest cure times in Figure 3 are all dense silica coated pigments. These also have the most acidic surfaces and the least ability to neutralise the PTSA. Hence, the cure time for these paints would be expected to be the shortest. The remaining pigments are more basic in nature and have more ability to neutralise the PTSA and hence produce longer curing times.

Following on from the results in Figure 3, the effect of cure time on gloss was studied in order to determine whether longer cure times would result in higher gloss due to better flow. Gloss values were measured and compared to the cure times. The results are given in Figure 4 where it can be seen that there is a good correlation.

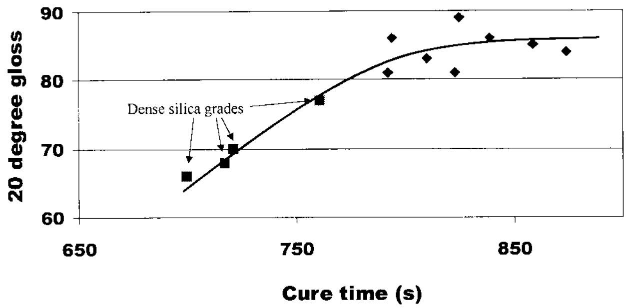

Figure 4. Effect of cure time on gloss in a PTSA catalysed paint system

Up to a point, an improvement in gloss can be achieved by increasing the cure time. However, once the cure time is more than ca. 800 seconds little improvement in gloss is evident. Obviously, for this particular formulation 800 seconds is sufficient time for optimal flow.

The square points in Figure 4 show the gloss values and cure times for the dense silica coated grades. Their shorter cure time has not helped the gloss performance. It should also be noted that the dense silica grades tended to have wider particle size distributions, which will also have a detrimental effect on the overall gloss performance.

Part 2 - Effect of PTSA Level on Cure and Optical Performance

To investigate the effect of PTSA level on cure and optical performance when using acidic and basic pigments, two further series of paints were prepared using the same formulation as above, but this time with varying PTSA levels. The first series was based on the predominantly basic pigment TIOXIDE TR81, which had resulted in the longest drying time and an excellent gloss performance in Part 1. The second series was based on G63/1, an acidic dense silica grade, which had resulted in the shortest cure time and poorest gloss performance in Part 1.

In Figure 5 the effect of PTSA level on the cure time for the two paint series is shown.

As would be expected from earlier results, TIOXIDE TR81 gives a substantially longer cure time than the dense silica grade G63/1. As the PTSA level is increased there is obviously more acid available to catalyse the cure resulting in shorter cure times for both pigments regardless of their surface treatment. The extent of reduction in cure time is similar for the two pigments.

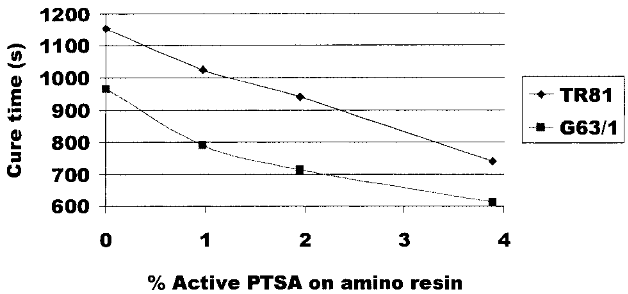

Figure 5. Effect of PTSA level on cure time

Solvent resistance and reverse impact testing of the paints related well to the cure results. The paints with 0% PTSA had a very poor solvent resistance and mechanical performance. With increasing PTSA levels, the solvent resistance and mechanical performance improved, showing G63/1, generally, to be slightly superior to TIOXIDE TR81.

In Figure 6 the effect of PTSA on the gloss performance of the two paint series is shown.

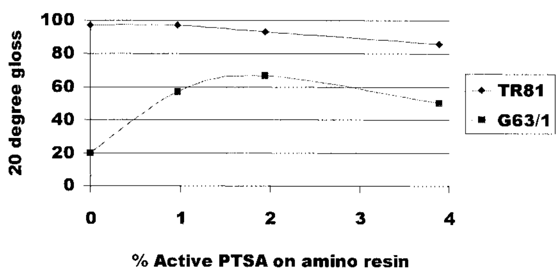

Figure 6. Effect of PTSA level on gloss performance

TIOXIDE TR81 and G63/1 reacted very differently to the increase in PTSA. The change in PTSA level affected TIOXIDE TR81 less than G63/1 and the gloss performance of TIOXIDE TR81 is significantly better than G63/1.

For TIOXIDE TR81, a slight decrease in gloss performance is noted. Referring to Figure 2, it is evident that by adding more acid to the system, poorer steric repulsion was expected for TIOXIDE TR81, which explains the poorer gloss at the higher PTSA levels. The faster cure time at the highest acid level could also be contributing towards poorer gloss.

Pigment G63/1 behaved quite differently. Regardless of the cure time decreasing with increasing PTSA level as shown in Figure 5, the gloss has initially increased quite substantially. The increased levels of acid could well be helping to improve the steric repulsion for this pigment (see Figure 1). However, at the PTSA level of 3.9% the gloss deteriorated, which suggests that the short cure time is now having a more dominant effect than the positive effect of having more acid present in the paint to improve steric repulsion.

To further investigate the results shown in Figure 6, pigment flocculation[7,8] was assessed using flocculation gradients. The flocculation data is given as a function of PTSA level in Figure 7.

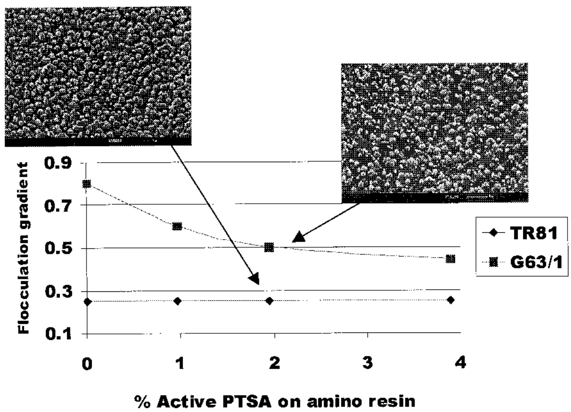

Figure 7. Effect of PTSA level on flocculation gradient

It is evident from Figure 7 that the dispersion of G63/1 is much more affected by changes in the PTSA level than TIOXIDE TR81 which has excellent flocculation stability with a consistent gradient below 0.30 suggesting that there is very little flocculation in these paints. From the results and the model in Figure 2, a slight deterioration in dispersion with increasing PTSA level would be expected for TIOXIDE TR81, however, this deterioration was not detected using the flocculation gradient technique.

For G63/1 the flocculation gradient varies from 0.80 to 0.44. The flocculation improves significantly with increasing levels of PTSA which relates well to the Figure 6 results and the model shown in Figure 1.

The illustrated micrographs for the paints with PTSA levels of 1.95% clearly support the flocculation gradient results.

In Figure 8 the opacity as a function of PTSA level is given, and, as with the gloss and flocculation gradient data, the opacity of TIOXIDE TR81 is significantly better than G63/1.

A slight decrease in the opacity level of TIOXIDE TR81 was observed as the PTSA level is increased, which agrees with the model in Figure 2. Similarly, the opacity of G63/1 generally improves with increased PTSA level, in line with the improvement in flocculation.

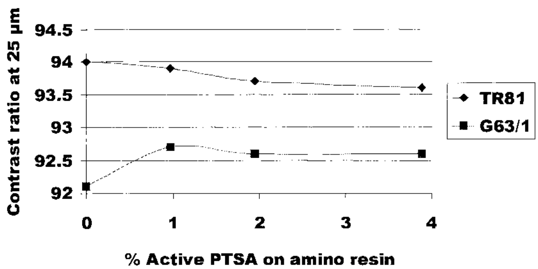

Figure 8. Effect of PTSA level on opacity performance

Part 3 - Effect of Resin Acidity on Cure Rate and Optical Performance in PTSA Catalysed Paints

Having seen how the PTSA level could significantly affect the cure rate and optical performance and how important TiO_2 choice was in this type of paint system, it was considered relevant to explore the effect of resin acidity on cure rate and optical performance.

For this purpose, a second PTSA catalysed paint system based on an alkyd resin was used. The alkyd was chosen for its high acidity (ie 20-25mgKOH/g cf 10mgKOH/g for the resin used in Part 2). From the model illustrated in Figures 1 and 2, this high acid resin would be expected to favour G63/1 more than the medium acid resin used in Part 2. Equally, the high acid resin would be expected to favour TIOXIDE TR81 less than the medium acid resin.

Cure rate, gloss, flocculation and opacity were assessed for both paint formulations at different PTSA levels using TIOXIDE TR81 and G63/1

In Figure 9 the cure time for TIOXIDE TR81 and G63/1 are shown for both the medium acid resin and the high acid resin, where it can be seen that the paint based on the high acid resin resulted in the fastest cure times, regardless of the TiO_2 used. The high acidity level appears to help catalyse the cure.

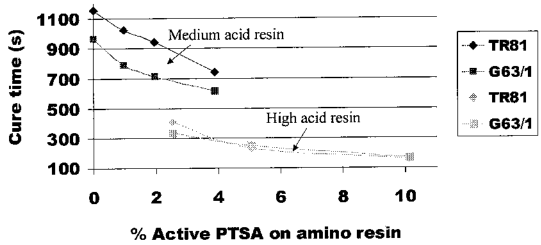

Figure 9. Effect of resin acidity and PTSA level on cure time

The other point to note, is that the high acid resin has brought the performance of G63/1 much closer to the performance of TIOXIDE TR81, compared to how the two pigments performed in the medium acid resin. The high acid resin does tend to be favouring G63/1 more than the medium acid resin. This relates well to the model in Figure 1.

As would be expected, as the PTSA level increases, more acid is available to catalyse the cure, hence the cure time decreases for both the medium and high acid resin systems.

In Figure 10 the effect of resin acidity and PTSA level on gloss can be seen for both paint formulations. The behaviour of the two pigments in the high acid resin system is similar in the tested PTSA range. G63/1 is now tending to follow the same model as TIOXIDE TR81 shown in Figure 2. This could be due to the high acid resin system having too much free acid available relative to the acidity of G63/1. In spite of G63/1 showing a similar trend and being closer in performance to TIOXIDE TR81 in the high acid resin system, the performance of TIOXIDE TR81 was still superior to that of G63/1.

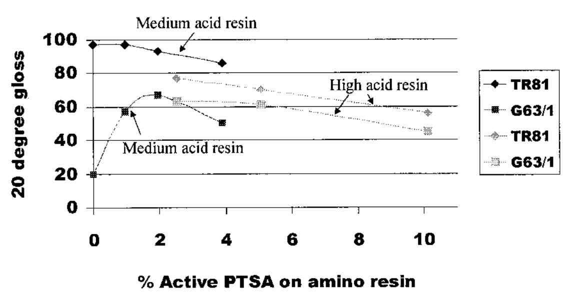

Figure 10. Effect of resin acidity and PTSA level on gloss performance

In Figure 11 the effect of resin acidity and PTSA level on pigment flocculation is shown for both paint formulations. It can be seen that the flocculation is worse in the high acid resin system than in the medium acid resin system. In both cases TIOXIDE TR81 shows the least flocculation.In contrast to the different behaviour of TIOXIDE TR81 and G63/1 in the medium acid resin system, the two pigments again showed similar trends in the high acid resin system, when the PTSA level is increased. A slight increase in flocculation was noted for both pigments.

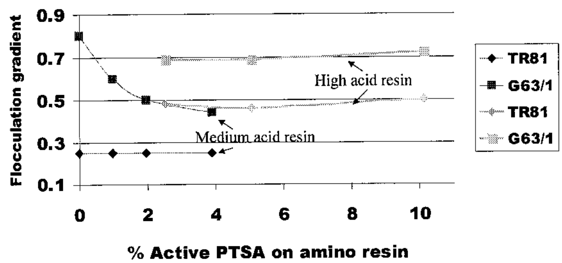

Figure 11. Effect of resin acidity and PTSA level on flocculation gradient

In Figure 12 the effect of resin acidity and PTSA level on opacity is shown for both paint formulations. It can be seen that the high acid resin reduced the performance difference between the two grades. However, TIOXIDE TR81 still performed the better.

Both pigments decreased slightly in opacity, which relates well to the slight increases in flocculation seen in Figure 11 for the high acid resin system. The fact that G63/1 is again following the same model for TIOXIDE TR81 as shown in Figure 2, again suggests that there is too much acid present in the high acid resin system relative to the acidity of G63/1.

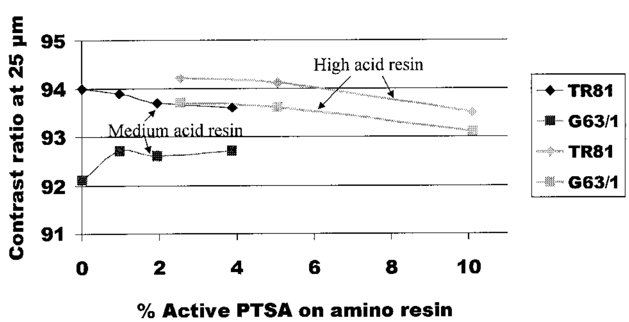

Figure 12. Effect of resin acidity and PTSA level on opacity performance

Conclusion

The paper has highlighted how the choice of TiO_2 affects the cure rate in a PTSA catalysed paint system. The more basic the TiO_2 pigment, the greater is the degree of neutralisation of the PTSA and increase in the cure time of the paint. For the paint systems tested, the basic TiO_2 pigments which resulted in the longest cure times also gave the best gloss performance, due to the longer cure time resulting in better paint flow.

The paper has highlighted how the choice of TiO_2 affects the cure rate in a PTSA catalysed paint system. The more basic the TiO_2 pigment, the greater is the degree of neutralisation of the PTSA and increase in the cure time of the paint. For the paint systems tested, the basic TiO_2 pigments which resulted in the longest cure times also gave the best gloss performance, due to the longer cure time resulting in better paint flow.

The resin acidity value was also found to be important for cure behaviour and optical performance. The high acid resin generally helped to improve the optical performance of the acidic pigment G63/1, as the steric repulsion was improved. In contrast the high acid resin generally resulted in a deterioration of the performance of the basic pigment TIOXIDE TR81. However, in spite of improving the conditions for G63/1, and deteriorating the performance of TIOXIDE TR81 by moving from a medium acid resin to a high acid resin, TIOXIDE TR81 still had the better optical performance.

Acknowledgements

The authors would like to thank the directors of Huntsman Tioxide for permission to publish this paper.

References

[1] T Entwistle and S J Gill, "*Effect of titanium dioxide pigments on the cure of thermosetting films*", Internal Huntsman Tioxide report D9200, **1985**

[2] C Bertrand, "*Titanium dioxide – Catalyst interaction: Review of results obtained with two types of high solids stoving enamel*", 15th FATIPEC Congress paper, Amsterdam, **1980**

[3] H Sander, "*The influence of titanium dioxide pigments on the rate of cure of acid catalysed one-component high solids baking paints*", Farbe und Lack, **1977**, 83, 891

[4] J E Hall, "*Pigment/resin interactions in thixotropic alkyd media*", Internal Huntsman Tioxide report D9163, **1982**

[5] K Goldsborough and J Peacock, "*The adsorption of alkyd resins by titanium dioxide*

pigments and its relation to the hiding power of alkyd paint systems", J. Oil Col. Chem. Assoc., **1971**, 54, 506-519

[6] J B Franklin, K Goldsborough, G D Parfitt and J Peacock, "*Influence of particle charge and resin adsorption on the opacity of paint films pigmented with titanium dioxide*", Journal of Paint Technology, **1970**, 42, 551

[7] D J Rutherford and L A Simpson, "*The use of a flocculation gradient monitor for quantifying pigment dispersion in dry and wet paint films*", Internal Huntsman Tioxide report D9186GC, **1984**

[8] J G Balfour and M J Hird, J. Oil. Col. Chem. Assoc., **1975**, 58, 331