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Steady-State Photodielectric Microwave Spectroscopy: Characterisation and Behaviour of Titanium Dioxide Pigments

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ABSTRACT

This paper reports on some recent findings in our current work carried out on an evaluation of the photoactivity and photoconductivity of titanium dioxide pigments using steady-state photodielectric microwave spectroscopy. The two crystalline forms of titanium dioxide, anatase and rutile with and without a surface coating are investigated. Each pigment exhibited a different microwave resonant frequency absorption profile, depending upon the nature of the crystalline modification and the presence of a surface coating. In this work, the effect of time, intensity and wavelength of irradiation and the temperature and humidity of the microwave cavity on the resonant frequency absorption changes of the pigments have been examined. Thus, on steady-state illumination of the pigments in the microwave cavity with polychromatic light the resonant frequency losses exhibited shifts, the nature of which were again dependent upon the pigment type and coating. The anatase pigments exhibited greater responses compared to the rutile pigments, particularly with regard to the shift in the resonant frequency values and the change in the Q factor of the resonant peak. The resonant frequency values of the anatase samples were also at higher values than those obtained for the rutile samples. Furthermore, the frequency shifts were in opposite directions, with the anatase modification exhibiting a more rapid shift to lower frequencies and rutile a slower shift to higher frequencies. It would appear that when the anatase samples were irradiated

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over a prolonged period of time the resonant peak reverts to a higher frequency value. Such processes are related to the differences in the thermodynamics of the crystal lattice. In the case of anatase, it is proposed that free charge carriers are produced on irradiation, whereas with the rutile form the energy input is only sufficient to cause excitation of the charge carriers to a higher energy level within the band gap, and this effectively introduces a space charge separation of the charge carriers, similar to that of an induced polarisation process. Coated pigments exhibited slower photo responses. In this case, the coating on the pigment particle surface is acting as a trap recombination centre. This process would reduce the number of charge carriers generated. An increase in the cavity temperature increases the photodielectric responses of both pigment modifications due to the promotion of charge carriers to higher energy levels, thus increasing the conductivity of the pigments. At higher temperatures rutile behaves like anatase. An increase in moisture had the reverse effect, due to the moisture on the surface of the pigment reducing its photoactivity by reacting with charge carriers, thus reducing the amount of photocurrent. The data are discussed in relation to the known photoactivity behaviour of titanium dioxide pigments in polymeric media. Preliminary data on other semiconductor materials such as selenium and zinc oxide, are also presented in the light of the above behaviour.

INTRODUCTION

The applications of pigments are now widespread, especially in the fields of microelectronics, xerography and solar energy conversion. In this regard, both inorganic and organic compounds have certain desirable properties to meet particular specifications, depending on the type of application.[1] This is particularly true of photoconductive compounds in xerography, where both inorganic and organic systems are being developed as photoreceptive layers for improved copying processes.[1-4] Indeed, since the first reports of photoconductivity in the 1930s and the application of fused sulphur to form electrostatic latent images, many compounds have been characterised, including several organic and inorganic dyes and pigments.[5-10] Whilst the basic mechanism of photoconduction is reasonably well understood in terms of the photogeneration, migration and recombination of carriers, the exact nature of the transport mechanism is somewhat controversial, particularly with regard to that of organic pigments and dyes.

We have recently undertaken studies on the photoconductive properties of organic halogenated anthanthrone pigments as vacuum deposited layers, and as dispersions in polymer films. These systems were found to be intrinsically photoconductive, with the charge-transport mechanism operating via a particle–particle contact. We developed an electrophotographic recording device based on the xerographic principle, in order to carry out such measurements.[11] More recently we have undertaken a detailed examination of the photoconductive properties of titanium dioxide pigments, with particular emphasis on their photoactivity in polymeric media and the nature of surface treatments. Here, thin films of titanium dioxide pigmented polyvinyl carbazole were found to be related to their photoactivities. In this regard the anatase and rutile forms of titanium dioxide were found to be markedly different, and these, in turn, were found to be influenced by the nature of the surface treatment.[12,13]

The common technique of photoconductive measurements involves the passage of current through the photoconductor in the dark, and monitoring the increase in the current when the photoconductor is irradiated and the current decay when the light is terminated. Other techniques have been reported; such as using electrodes made from the photoconducting materials,[14,15] or using the flash photolysis method on the photoconductor[16] dispersed in a solvent.

Although the dielectric behaviour of many materials has been reported, the simple measurement technique involving capacitors has been found, in our work, to be unsuitable for powdered materials. It is also difficult when examining the effect of irradiation on the sample. On the other hand, microwave dielectric spectroscopy is a relatively recent technique available for the examination of granular and powder type materials. One of the established uses of this technique is the moisture measurement of samples, as water molecules (free or bound) exhibit significant absorptions's in the microwave regions.[17,18] The photodielectric behaviour of CdS has been reported,[18] from which significant changes were observed in the signal when the sample was illuminated.

In our recent work, a simultaneous examination of titanium dioxide pigments using the technique of microwave dielectric spectroscopy gave a good correlation between absorbed microwave energy (as return frequency loss) and pigment photoactivity. This initial finding was extremely interesting, in that not only did it provide a rapid method for the early prediction of pigment photoactivity but also proved to be a novel technique for gaining a deeper understanding of the nature of the factors responsible for initiating and controlling pigment durability.[12] In turn, these results were closely allied to those obtained through photoconduction where there were marked differences in the behaviour of the anatase and rutile crystalline forms of the oxide. Thus, the more photoactive pigments, such as uncoated anatase and rutile, gave less frequency losses and were more photoconductive in terms of carrier recombination in thin films of poly(N-vinylcarbazole) than the less photoactive coated pigments, where greater frequency losses were observed combined with lower photoconductivity.

Following this work, a preliminary study into the microwave return frequency losses of titanium dioxide pigments was carried out under the influence of polychromatic light.[13,19] From this investigation, three interesting features were observed. First, on illumination the return frequency losses underwent a shift. Secondly, the degree of shift was dependent upon the photoactivity of the pigment and the nature of the surface treatments, and thirdly, the direction of the shift (+/−) was dependent upon the crystalline modification of the oxide pigment.

A number of earlier studies on inorganic semiconductors using microwave spectroscopy have been used to measure changes in their conductivity, but only on pulsed illumination.[20-24] For example, changes in microwave energy with an increase in conductivity of a material have been associated with the reflection of microwave energy back to the source rather than absorption. On this basis, if a material became more conductive, the power loss from the source would be reduced.

Our preliminary studies indicated that only materials with photoconductive properties exhibit photodielectric shifts. Current photoconductivity theory for photoconductive materials such as ZnO and CdS under these conditions is consistent with consideration as a dielectric material in a capacitor across an alternating field. In the microwave region, polarisation effects are observed. In the absence of light, changes in initial resonant frequency are observed with very low levels of dopants indicating that the dielectric behaviour of pigments is sensitive to small changes in crystal structure. On illumination, changes in lattice dispersion are then observed, due to free carrier dispersions and the filling of carrier traps, thus increasing the apparent dielectric constant of the capacitor.[1,14] From the photodielectric behaviour of the pigments, it would appear that the dielectric property of each crystalline form (coated and uncoated) is different.

The significance and novelty of our observations led us to investigate this technique and the photodielectric phenomena further. Typical nonconductive materials (organic and inorganic) were found to be unresponsive, suggesting that there are distinct differences in the photoconductive properties of the two crystalline modifications of titanium dioxide pigments. Thus, to elaborate on the mechanisms involved, we have studied the photodielectric properties of titanium dioxide pigments (uncoated and coated) further with regard to the effects of time, light intensity and wavelength and humidity. The technique has also been extrapolated to a study of other photoconductive compounds and found similar interesting results that could improve our understanding of the technique.

The use of titanium dioxide pigments in industry often involves the incorporation of the pigment into polymeric materials. The photocatalytic degradation of these pigmented polymers has been associated with the photoactivity of the pigments and the adsorbed species on the pigment surface. Whereas the anatase form has been reported to be photoactive, the rutile form is relatively inert.[11-13] The current method for the evaluation of the durability of pigmented polymer materials depends on the actual or accelerated artificial weathering technique used, which tends to be time consuming and tedious. From much of the work carried out to date in this area, it appears that the photoactivity of the pigment is directly related to the photodegradation rate of the polymer.[25] In this regard many model system studies have been investigated to provide rapid and reliable information on such degradation phenomena.[26] The results on photodielectric microwave spectroscopy makes a significant contribution to our understanding of such photoactivity behaviour in polymeric media.

EXPERIMENTAL

Materials

The pigments examined were uncoated and coated samples of anatase and rutile and were supplied by Tioxide Group Services Ltd, Billingham (UK). Samples of zinc oxide, cadmium sulphide and selenium were also supplied by the same company. The coatings used were silica/alumina based. The salts, cobalt chloride, nickel sulphate, copper sulphate, chromium chloride, ferric sulphate, potassium permanganate, ammonium sulphate, sodium bromide, potassium carbonate and calcium chloride were all obtained from BDH Co. Ltd, Poole, UK.

Microwave dielectric measurements

The instrumentation consisted of a Marconi 2–20 GHz Programmable Sweep Generator 6310 coupled to a Marconi Automatic Amplitude Analyser 6500, and to a Hewlett Packard 7475A Plotter.

The pigment samples (1 and 2 g each) were evenly distributed over a Perspex holder, and placed into a cylindrical cavity resonator. The resonant frequency of the sample was located and this was monitored when the sample was irradiated at regular intervals up to 30 min and for the same period when the irradiation ceased. The light source was provided by a Rank Aldis projector with a tungsten light bulb (24 V 250 W).

The measurements were the resonant frequency value f_{min} and the dielectric loss or Q factor, which are related by the expression $Q = f_{min}/\delta f$, where δf is the frequency difference at half the peak height.

Light intensities were controlled by fitting a dimmer control to the projector lamp and were measured using a Newport Digital Power Meter (Model 815 Series). Dimmer controls from 4 through to 10 inclusive had intensity readings of 1, 2, 6, 9, 14, 15·2 and 17·6 mW respectively. The following filter solutions at 0·05 M concentration were also used; 1-Control, 2-Distilled water, 3-$CoCl_2$, 4-$NiSO_4$, 5-$CuSO_4$, 6-$CrCl_3$, 7-$Fe_2(SO_4)_3$, 8-$KMnO_4$.

The relative humidity of the cavity was modified using the following saturated solutions and dried solids and was measured using a Fisher type III Hair Hygrometer:

Satd ammonium sulphate	77% RH at 25°C
Satd sodium bromide	63% RH at 25°C
Satd potassium carbonate	55% RH at 25°C
Solid calcium chloride	30% RH at 25°C

The cavity and the light source were enclosed using a clear polyethylene sheet and the relative humidity was monitored until an equilibrium was reached and the resonant frequency value of the cavity was then located. The sample of pigment was then introduced into the cavity and allowed to attain an equilibrium.

The temperature of the cavity was changed using a Gallenkamp heater and was recorded using an RS Components Digital Thermometer No. 610067. The resonance frequency of the empty cavity was monitored with temperature increase. The sample was allowed to reach thermal equilibrium for 30 min in the cavity before irradiation was commenced. Temperatures were controlled at 56, 76 and 107°C.

RESULTS

Photodielectric effect

The photodielectric behaviour of the four pigment samples in the cavity cell are summarised in Fig. 1. As discussed previously[12,13] the resonance frequency value of the empty cavity containing the Perspex holder was found to be higher compared with those obtained with the pigment samples. The change in the resonant frequency is related to the interaction of the sample with the electric field component of the cavity mode. The resonance frequency value of each pigment was found to be dependent on the sample size and varied with the pigment examined. For comparative purposes

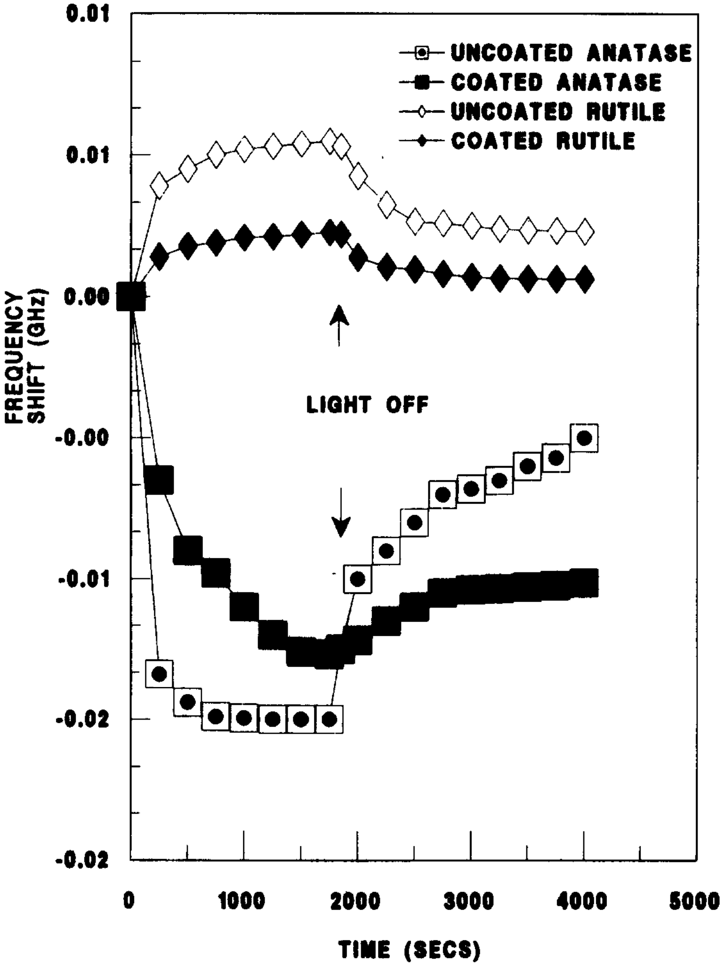

Fig. 1. Resonance frequency shifts for 2 g samples of (☐) uncoated anatase, (■) coated anatase, (◇) uncoated rutile and (◆) coated rutile pigments in the sample cavity with time of irradiation.

here 2 g sample weights were used, except for all further data where only 1 g sample weights were used.

For the anatase samples, it was noted that the resonant frequencies moved toward lower frequency values when the samples were irradiated, with the uncoated sample exhibiting a faster response than the coated sample. In our earlier work,[12,13] the half-life of the photodielectric response was also found to increase linearly with the sample size, for both coated and uncoated anatase pigments.

The sharpness of the resonant peak, i.e. an indirect measurement of the dielectric loss, was found to decrease with the time of irradiation, and

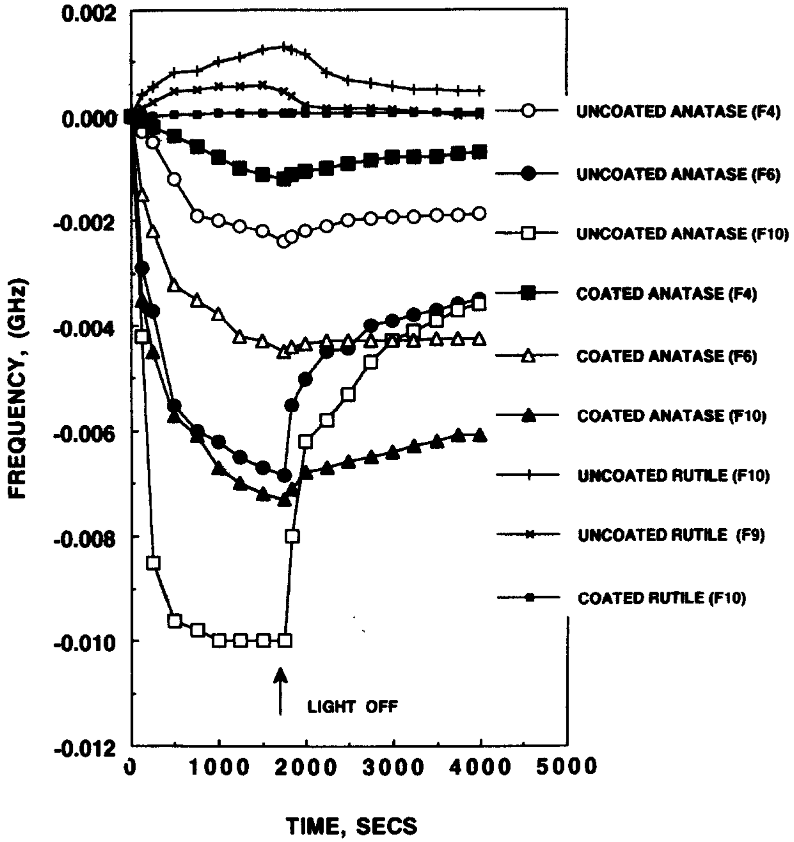

Fig. 2. Resonance frequency shifts for 1 g samples of (○)F4, (●)F6, (□)F10 uncoated anatase, (■)F4, (Δ)F6, (▲)F10 coated anatase, (×)F9, (+)F10 uncoated rutile and (⊞)F10 coated rutile pigments at various light intensities.

gradually return to its original higher frequency value when the illumination was terminated, as illustrated in Fig. 1. Furthermore, the recovery rate of the uncoated pigment was faster than the coated sample, as shown by the dark decays.

For the rutile samples, it was found that when the sample is irradiated, the shift in the resonant frequency is toward higher frequency values, which is in the opposite direction to that obtained for the anatase samples. These results are illustrated in Fig. 1 for uncoated and coated rutile pigments respectively. The uncoated rutile pigment exhibited a greater shift in the resonant frequency than the coated sample for the initial values compared to that of the control and also those produced on irradiation. A less obvious change in the peak sharpness for the rutile pigments was also observed, compared to that of the anatase samples.[12,13] The coated rutile pigment also exhibited a slower photoresponse than

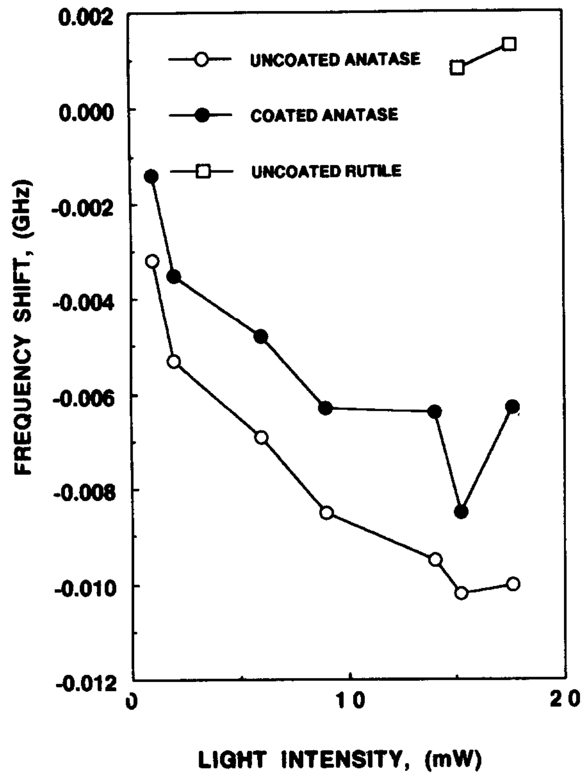

Fig. 3. Maximum resonance frequency shifts for (○) uncoated anatase, (●) coated anatase and (□) uncoated rutile on irradiation in the sample cavity with different light intensities.

that of the uncoated rutile, while the effect is reversed in the dark decays. In comparison with the anatase pigments discussed above, the uncoated anatase exhibits the fastest photodielectric resonant frequency shift and this may be associated again with its higher photoconductivity.

Effect of light intensity

Changes in the resonance frequency shift with light intensity are shown in Fig. 2 for all four pigment types. For the uncoated anatase, the amount of change in the resonance frequency decreased with a corresponding decrease in the light intensity. The rate of the shift in the resonance frequency was also retarded. Similar observations were made on the coated anatase sample, but in this case the rate and amount of frequency shift was much less with irradiation time. For convenience, filter numbers F4, F6 and F10 are shown in Fig. 2.

For the uncoated rutile pigment however, although the frequency shift

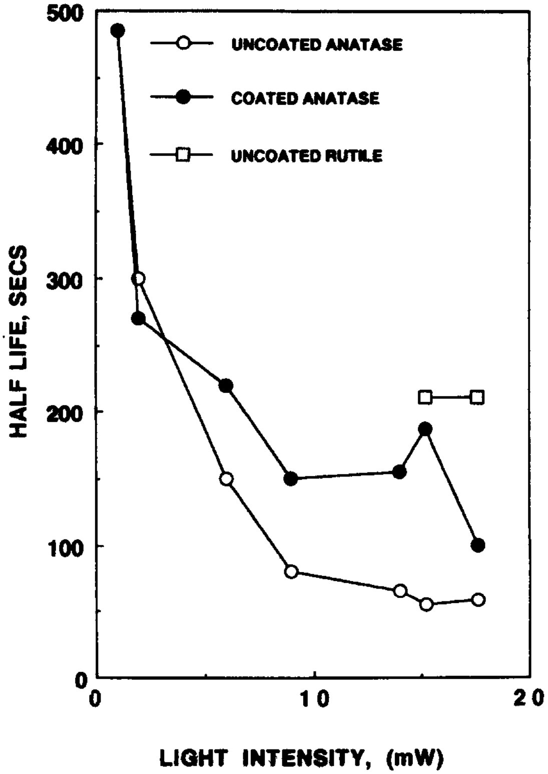

Fig. 4. Half-lives of resonance frequency shifts for (○) uncoated anatase, (●) coated anatase and (□) uncoated rutile on irradiation in the sample cavity with different light intensities.

and the rate of photoresponse followed the above trends, but in reverse, it is only possible to observe the photodielectric effect at the higher intensity scales of F9 and F10. For the coated rutile pigment only negligible changes were observed at the F10 scale. The relative effects of the maximum degree in frequency shifts are shown in Fig. 3. The effects are seen to be greater for uncoated than coated anatase pigments, with the effect diminishing with decreasing light intensity. The uncoated rutile shows little change at the positive end of the frequency shift scale. The half-lives of the frequency shift show the same trends as can be seen from the data in Fig. 4. Here, the uncoated anatase exhibits a faster photoresponse with increasing light intensity, compared with those of the coated rutile pigment.

Effect of wavelength

The effects of narrow bands of light energy from a monochromator and xenon arc source (150 W) were found to be insufficient to excite the sample

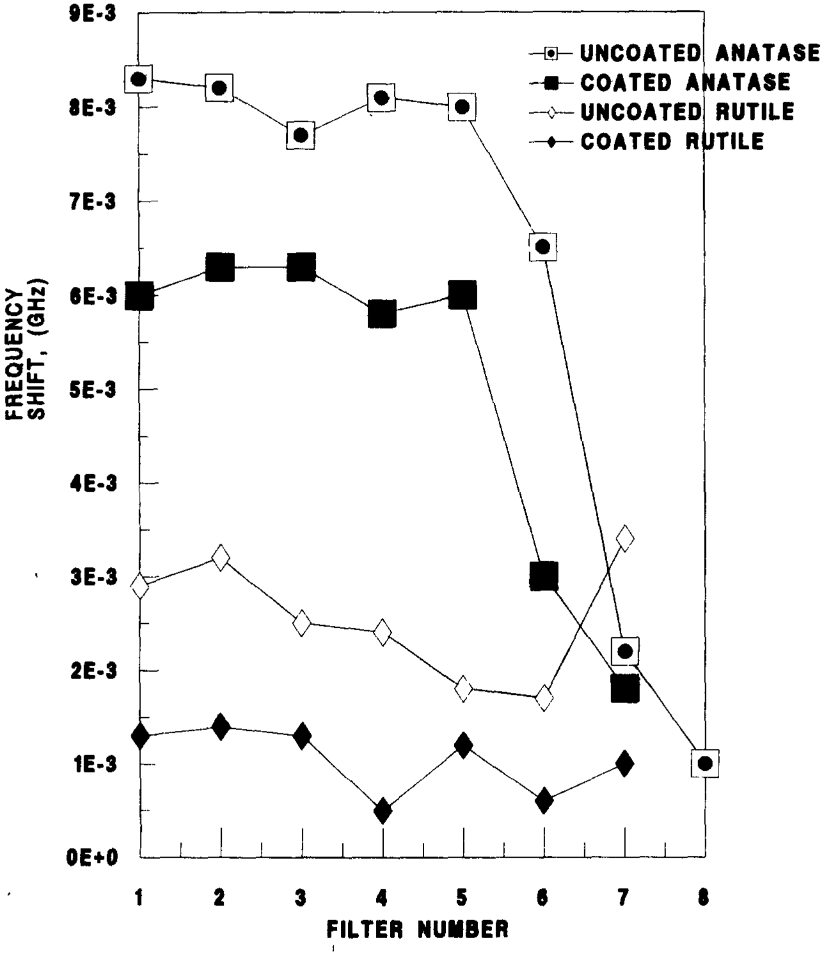

Fig. 5. Maximum resonance frequency shifts for (□) uncoated anatase, (■) coated anatase, (◇) uncoated rutile and (◆) coated rutile on irradiation in the sample cavity with wavelength filters.

arrangement used in this study. Light filter solutions were therefore used, but at the same time realising, that apart from proving some degree of wavelengh selectivity in terms of regions of light energy, the light intensity is also affected. Relative frequency shifts for the four pigment samples, for the different filter solutions, are shown by the data in Fig. 5. Surprisingly, the frequency shifts were found to be fairly consistent up to filter number 6. The only difference between numbers 1 and 2 is the infra-red radiation, which obviously has a negligible effect here. Filter number 3 transmits all the UV light up to 450 nm while number 4 transmits light up to 400 nm and above 500 nm. Filter number 5 absorbs all the UV light below 350 nm, while number 6 transmits UV light between 300 and 450 nm and visible

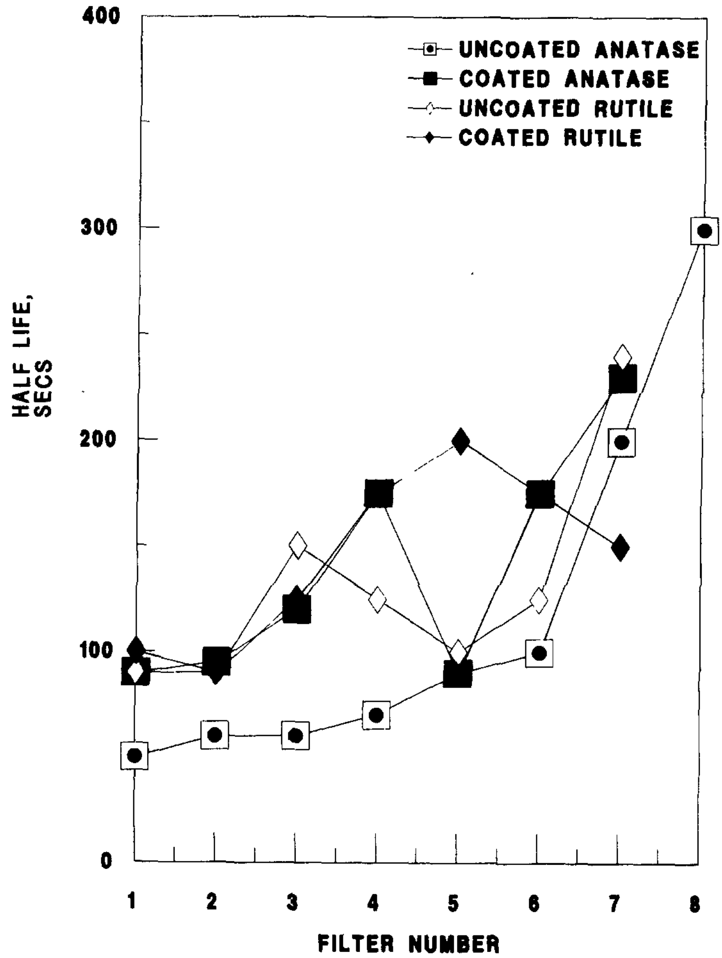

Fig. 6. Half-lives in resonance frequency shifts for (□) uncoated anatase, (■) coated anatase, (◇) uncoated rutile and (◆) coated rutile on irradiation in the sample cavity with wavelength filters.

light between 500 and 600 nm. From this data therefore it would appear that the pigments have strong near UV activity in the region 350–405 nm. The use of filter number 7 absorbs all light below 500 nm and a rapid decrease in frequency shift is seen for all four pigments. The same applies to filter number 8, where light energies between 400 and 500 nm are transmitted and only the uncoated anatase appears to exhibit any photoresponse. The half-lives of the photo decays show a similar effect (Fig. 6) and increase gradually up to filter number 6, thereafter decreasing rapidly with filter numbers 7 and 8. Again, only the uncoated anatase responds to filter number 8.

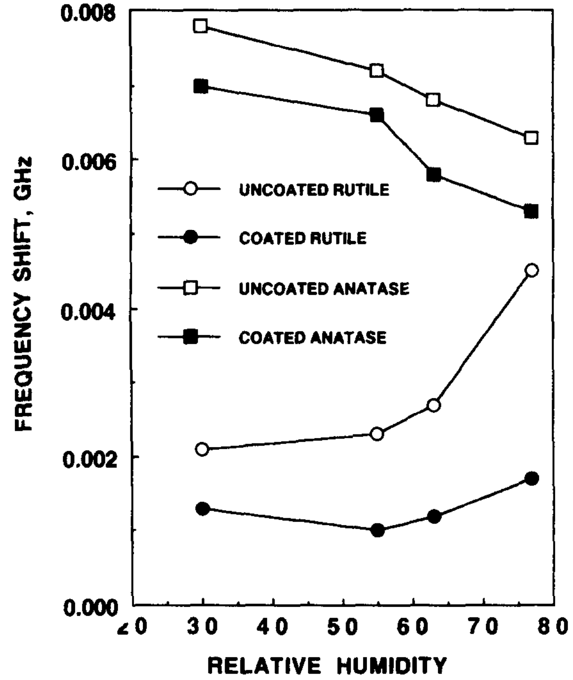

Fig. 7. Maximum resonance frequency shifts for (□) uncoated anatase, (■) coated anatase, (○) uncoated rutile and (●) coated rutile on irradiation in the sample set at different humidities.

Effect of humidity

The effect of humidity on the photodielectric response of the four pigment samples is shown in Fig. 7. For the anatase samples, it is seen that as the relative humidity of the cavity chamber increases, so the frequency shift decreases. However, with the rutile samples the effect was reversed, in that the frequency shift increased with increasing relative humidity. The photodielectric half-life values are compared in Fig. 8. In this case the half-lives for the frequency response of the anatase samples remain virtually unaffected by changes in relative humidity, except for a small increase for the coated anatase at higher relative humidities. On the other hand for the rutile pigments, the half-lives of the frequency shift decreased with increasing relative humidity.

Effect of temperature

Studies on temperature effects proved to be quite complex. Over the temperature range studied, both resonance frequency value and the Q factor for the cavity changed significantly. This was due to the physical

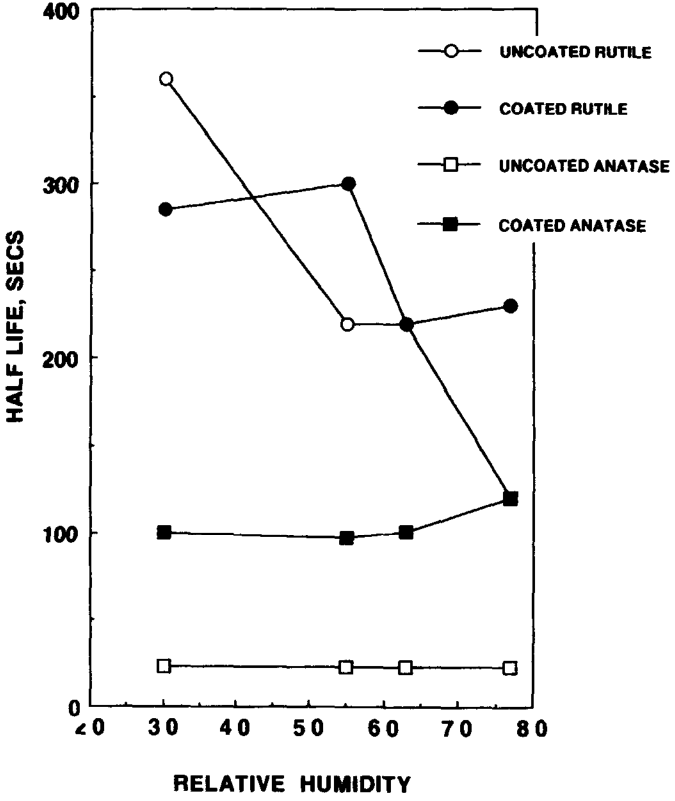

Fig. 8. Half-life of resonance frequency shifts for (□) uncoated anatase, (■) coated anatase, (○) uncoated rutile and (●) coated rutile on irradiation in the sample cavity set at different humidities.

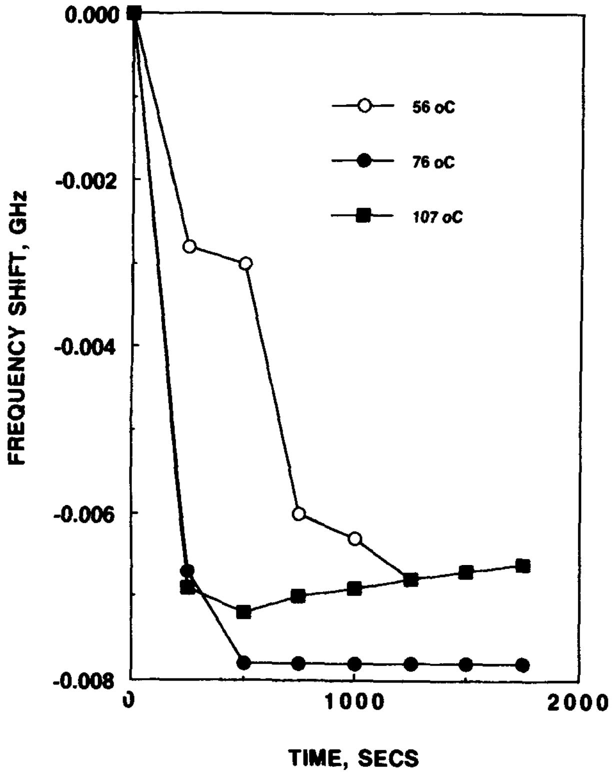

Fig. 9. Photodielectric shifts for uncoated anatase pigment at (○) 56°C, (●) 76°C and (■) 107°C on irradiation in the sample cavity with time.

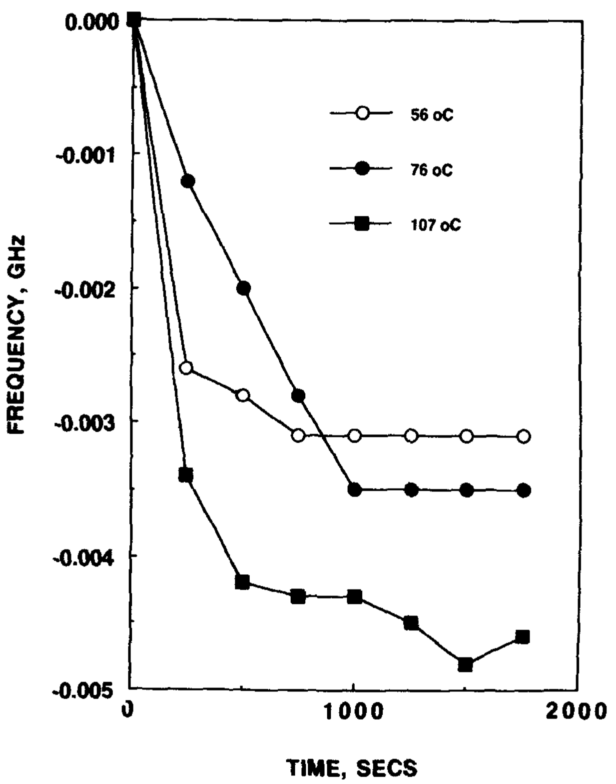

Fig. 10. Photodielectric shifts for coated anatase pigment at (○) 56°C, (●) 76°C and (■) 107°C on irradiation in the sample cavity with time.

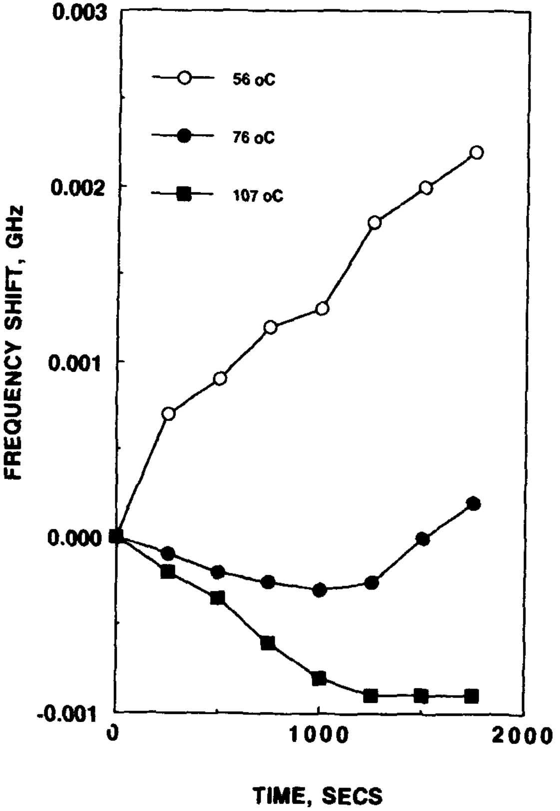

Fig. 11. Photodielectric shifts for uncoated rutile pigment at (○) 56°C, (●) 76°C and (■) 107°C on irradiation in the sample cavity with time.

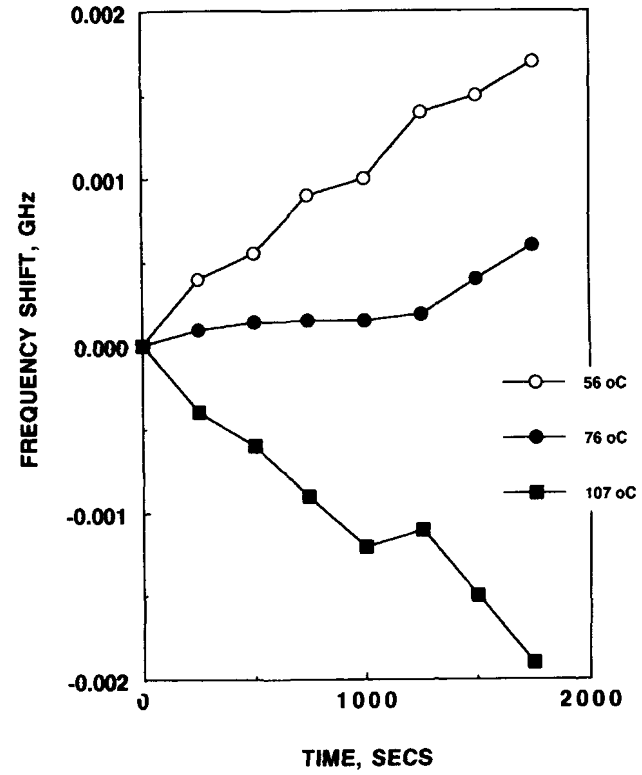

Fig. 12. Photodielectric shifts for coated rutile pigment at (○) 56°C, (●) 76°C and (■) 107°C on irradiation in the sample cavity with time.

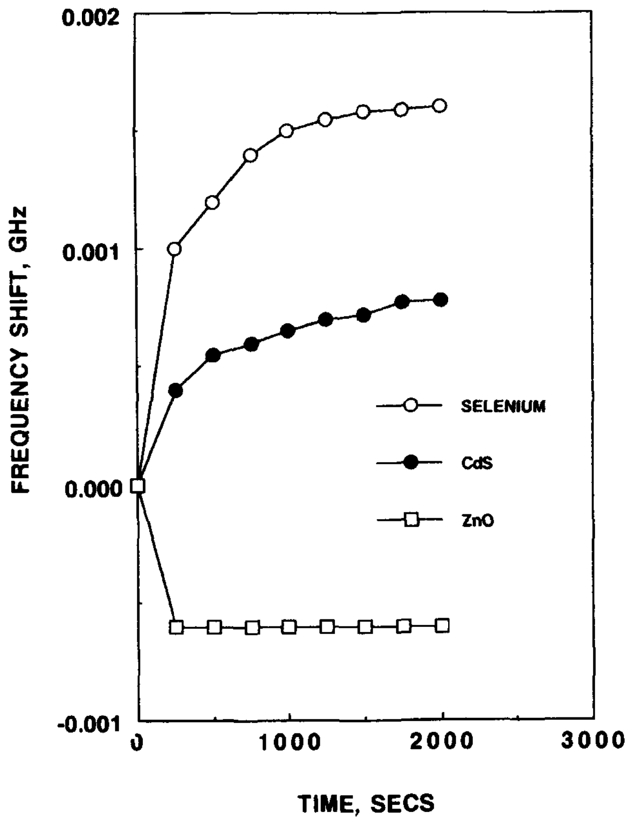

Fig. 13. Photodielectric shifts for (○) Se, (●) CdS and (□) ZnO on irradiation in the sample cavity with time.

property changes of the brass cavity wall with heating. Both the conductivity and size of the cavity increased with increasing temperature. At first the anatase samples appeared to exhibit a decrease in frequency shift on irradiation with an increase in temperature, whereas the rutile samples showed virtually no change. This observation, however, altered significantly when changes in the cavity wall were taken into consideration.

The real changes in the photodielectric shift with irradiation time are shown in Figs 9–12 for the four respective pigments. Figures 9 and 10 show the respective frequency shifts for uncoated and coated anatase pigments at 56, 76 and 107°C. It is seen that the frequency shifts increase markedly with increasing cavity temperature, the effect being greater for the former pigment. With the rutile pigments the frequency shift with irradiation time changed from a positive shift (toward a higher frequency) to a negative shift (toward a lower frequency) with increasing temperature (Figs 11 and 12). This effect was gradual at intermediate temperatures.

Other semiconductors

The photodielectric shifts for selenium, cadmium sulphide and zinc oxide are shown in Fig. 13 for comparison purposes. Both selenium and cadmium sulphide behaved in the same way as rutile, while zinc oxide exhibited the same properties as anatase. All three materials were obtained in high purity grade form.

DISCUSSION

Differences in the photodielectric responses of anatase and rutile are evidently associated with the difference in their crystalline form (Figs 1 and 2). However, the former pigment is also significantly more photoactive, suggesting that the two modifications have different conduction mechanisms, both of which are influenced by the nature of the surface treatment on the pigment particle.

In the case of the anatase samples, there was not only a shift in the resonance frequency peak with irradiation time, but also a peak broadening. Thus, as the Q value decreases during irradiation, the microwave power loss decreases. However, on prolonged irradiation, the opposite changes began to occur for the anatase samples, i.e. the resonant peak eventually moved to higher frequency values, narrowed and the power loss increased. This reversed change for the anatase pigment samples occurred over a considerably longer period of time, and at a much slower rate than the initial changes (i.e. over 2–3 h). Thus, at much longer irradiation periods the anatase samples reverted to the same property changes as those of rutile. For the rutile pigments the initial changes on irradiation were opposite to those of anatase and much slower. However, no further changes in frequency shift were observed over very prolonged irradiation periods. Such changes in the anatase form were not noted previously.

The differences in photodielectric behaviour between the two crystalline forms of titanium dioxide seem to suggest that there are two different types of electronic processes taking place. Thus, during the photoconduction process in anatase, the photocurrent produced would cause a distortion of the miocrowave electric field during the early stages. When all the carriers are freed, the continued irradiation would provide the necessary energy to maintain charge separation. This would then induce a polarisation effect within the pigment particle and the bulk of the sample, which may then re-align with the microwave electric field, thus accounting for the reversed changes over a prolonged period of time.

In the case of the rutile pigment, it is possible that the irradiation energy is insufficient to generate charge carriers due to the close packing in the crystal lattice. However, the energy may have been sufficient to promote electrons to a higher energy level in the band gap closer to the conduction band and thus produce a polarisation effect within the crystal lattice. This effect will then interact with the electrical field of the microwave cavity.

One other observation which also suggests that the crystal lattice affects the nature of the energy levels present in the band gap is that of the photodielectric half-lives. The relatively short half-lives of the anatase samples, compared with those of rutile, suggests that the latter either have more energy levels or deeper energy levels in the band gap. In the latter case more energy would be required to release the charge carriers from the energy level.

Differences in the photodielectric behaviour of the two crystalline modifications is further highlighted by the effects of light intensity (Figs 3 and 4). These results showed that while the anatase samples were active at lower light intensities, the rutile samples were non-active. In fact, the rutile pigments were even non-active at relatively high light intensities. This effect would appear to confirm that differences in the crystalline lattice of the two forms of pigment lay in the differences in the properties of the pigment band models, i.e. differences in the types of energy levels in the band gap.

From an examination of the data on the effects of different filter solutions (Figs 5 and 6), the phenomenon observed appears to be solely that of photoconduction activation by the UV region between 350 and 400 nm. This covers the low energy absorption profiles of the two titanium dioxide pigment forms.

It was predicted that the amount of moisture present in a pigment sample would have a significant influence on its photodielectric behaviour, since moisture absorbs strongly in this region of the electromagnetic spectrum (Figs 7 and 8). An increase in the moisture content would therefore increase the amount of adsorbed water on the pigment particle surface. Photogenerated carriers from the pigment would then react with the water molecules, thus producing reactive radicals which would, in turn, react with the opposite charge carriers and hence reduce the amount of photocurrent. With the anatase samples an increase in the moisture content was found to reduce the photodielectric changes, whereas for rutile pigments the changes had increased. In the latter case, the increased polarisation of the water molecules would increase the degree of polarisation in the pigment, thus increasing the photodielectric shift.

Studies on the effect of temperature had revealed that an increase in the temperature will increase the conductivity of the material due to the promotion of charge carriers to a higher energy level by thermal excitation (Figs 9–12). Using this information, it was found that an increase in temperature does increase the photodielectric effect for anatase, probably due to its greater photoactivity. Rutile pigments, on the other hand, also exhibited photodielectric changes similar to those of anatase at higher temperatures. Thus, the photoactivity and photoconductive properties of rutile increase with increasing temperature.

The study on other semiconductors was interesting in that selenium, a well known photoconductor, exhibited similar behaviour to that of rutile, as did cadmium sulphide (Fig. 13). Zinc oxide on the other hand behaved in the same way as anatase but at a faster rate, i.e. shorter half-life.

An examination of the power loss from the anatase sample absorption peak showed that there was a tendency for more power to be reflected back to the source with irradiation time. This suggests that the pigments had become conductive, thus reflecting the microwaves back to the source. The rutile samples on the other hand exhibited an increase in absorption power on irradiation except at higher temperatures. Thus, on irradiation, it would appear that the light energy is sufficient only to promote electrons into some lower lying energy level, but not the conduction band. As the temperature is increased the thermal energy is sufficient to promote the electrons from the energy level in the band gap to the conduction band.

CONCLUSIONS

It would appear from the results that the two crystalline forms of titanium dioxide exhibit a different microwave resonant frequency absorption profile depending upon the nature of the crystalline modification and the presence of a surface coating. On steady-state illumination of the pigments in the microwave cavity with polychromatic light, the resonant frequency losses exhibit shifts, the nature of which also appear to be dependent upon the pigment type and coating. The anatase pigments exhibited greater responses compared to the rutile pigments, particularly with regard to the shift in the resonant frequency values and the change in the Q factor of the resonant peak. The resonant frequency values of the anatase samples are also at higher values than those obtained for the rutile samples. Furthermore, the frequency shifts are in opposite directions, with the anatase modification exhibiting a more rapid shift to lower frequencies and rutile a slower shift to higher frequencies. It would appear that when the anatase samples are irradiated over a prolonged period of time, the resonant peak reverts to a higher frequency value. Such processes are related to the differences in the thermodynamics of the crystal lattice. In the case of anatase it is proposed that free charge carriers are produced on irradiation, whereas with the rutile form, the energy input is only sufficient to cause excitation of the charge carriers to a higher energy level within the band gap, and this effectively introduces a space charge separation of the charge carriers, similar to that of an induced polarisation process. Coated pigments exhibited slower photoresponses. In this case the coating on the pigment particle surface is behaving as a trap recombination centre. This effect would reduce the number of charge carriers generated. An increase in the cavity temperature increases the photodielectric responses of both pigment modifications due to the promotion of charge carriers to higher energy levels, thus increasing the conductivity of the pigments. At higher temperatures rutile behaves like anatase due to the thermal excitation of charge carriers to the conduction band. An increase in moisture had the reverse effect due to the moisture on the surface of the pigment reducing its photoactivity by reacting with charge carriers, thus reducing the amount of photocurrent. The data are interesting in relation to the known photoactivity behaviour of titanium dioxide pigments in polymeric media. The relative inactivity of rutile pigments compared with that of anatase is evidently due to the higher photoconductive properties of the latter. Surface treatments are also important in reducing pigment photoactivity by behaving as electron traps as well as screening the incident radiation. Recent work on the photoactivity of a range of titanium dioxide pigment types in polyolefins[25] showed that the photoactivity of rutile pigments increased with increasing temperature of irradiation. In view of our findings here, it would appear that this effect is consistent with the enhanced photoconductivity of the rutile with increasing temperature.

Finally, surface and bulk effects of the pigment particles are difficult to distinguish from this data, although it is likely that the former are predominant under these experimental conditions. Future work will entail the development of pulsed photodielectric microwave spectroscopy with a smaller cavity and specially prepared pigments, which will hopefully unravel the complexities of the bulk and surface processes involved.

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