Dyes and Pigments **20** (1992) 211–226

Electrophotographic and Microwave Photodielectric Studies (I) Effect of Various Transition Metal Dopants on Titanium Dioxide Pigments in the Solid State

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(Received 1 June 1992; accepted 3 July 1992)

ABSTRACT

Several titanium dioxide pigments in the rutile crystalline form have been doped with Ni, Co, Fe, Pb, Cu, V and Mo ions by co-precipitation in aqueous alkaline solution with titanium (IV) chloride. The photoconductivities in thin poly(vinyl carbazole) films and photodielectric microwave responses of the various transition-metal-doped titanium dioxide pigments have been measured and are discussed in terms of their photoactivities. The results suggest that different dopants affect the photoconductive and photodielectric responses of the titanium dioxide pigments to different extents. Photoconductive responses of the rutile pigments measured electrophotographically are enhanced on doping with the metal ions, and these responses increase with increasing concentration. Using microwave spectroscopy, the initial resonant frequency return loss decreases with a magnitude which is dependent upon the type and concentration of the cation. On steady-state illumination, the half-life of the photodielectric shift of the resonant frequency return loss is reduced, i.e., is more facile after doping, with the same order as that observed electrophotographically. The results are discussed in terms of the dopants occupying interstitial Ti(IV) sites in the crystal lattice and behaving as traps for photogenerated holes, thus reducing the photoactivity of the pigment.

1 INTRODUCTION

The applications of pigments are now widespread, especially in the fields of microelectronics, xerography and solar energy conversion. In this re-

Dyes and Pigments 0143-7208/92/$05.00

gard, 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.[11] These systems were found to be intrinsically photoconductive, with the charge-transport mechanism operating via 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, the nature of surface treatments and crystalline modifications. Here the photoconductivities of thin films of titanium-dioxide-pigmented poly(vinyl carbazole) were found to be related to their photoactivities. In this regard the anatase and rutile forms were found to be markedly different and these, in turn, were found to be influenced by the nature of the surface treatments on the pigment particle surface.[12,13].

This programme of work also utilised microwave dielectric spectroscopy for the determination of moisture in materials and a simultaneous examination of titanium dioxide pigments gave a good correlation between absorbed microwave energy (as return frequency loss) and pigment photoactivity. This initial finding was extremely interesting in that it provided a rapid method for the early prediction of pigment properties and their photoactivity. In turn, these results were closely allied to those obtained through photoconduction, where marked differences in the behaviour of the anatase and rutile crystalline forms of the pigment were also observed.

Following this work, a preliminary study of the microwave return frequency losses of titanium dioxide pigments under the influence of polychromatic light was carried out. From this investigation three interesting features emerged. Firstly, on illumination the return frequency losses underwent a shift. Secondly, the degree of shift was dependent upon the photoactivity of the pigment and nature of the surface treatments and thirdly, the direction of the shift (+/−) was dependent upon the crystalline modification of the pigment. In this regard the changes in the resonant frequency values are related to the interaction of the sample with the electric field component of the cavity which is, in turn, dependent upon the sample size, achieving a maximum and plateau at a particular weight of sample for cavity system. For anatase pigments, the resonant frequencies were found to move toward lower frequency values on irradiation, with the uncoated pigment exhibiting a faster response than the coated pigments. The sharpness of the resonant peak was found to be an indirect measure of the dielectric loss of the pigment and was found to decrease with time of irradiation and then return to its original state upon termination of the illumination, with uncoated pigments responding much faster than coated pigments.

Our preliminary studies indicated that only materials with photoconductive properties exhibited photodielectric shifts. Current theory for photoconductive materials such as ZnO and CdS under these conditions is consistent with the consideration of a dielectric material in a capacitor across an alternating field. In the microwave region lattice dispersions are observed. In the absence of light, changes in initial resonant frequency return losses 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 further changes in lattice dispersion are 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 for anatase the dielectric properties change from a conductor-like to an insulator-like material upon illumination. In the case of rutile pigments the effects are reversed, with uncoated pigments exhibiting a more significant shift in the resonant frequency than coated pigments, suggesting that coatings/impurity traps play an important role in controlling both pigment photoactivity and conductivity. One may speculate that the anatase pigments are absorbing more energy from the microwave source in order that the crystal lattice may obtain a more 'stable' structure, although one may not expect such a process to be reversible.

Titanium dioxide is one of the most widely used white pigments in industrial applications. The popularity of the pigment is influenced by some of its properties, such as a high refractive index, tinting strength, chemical inertness, thermal stability and non-toxicity. The use of titanium dioxide pigments in industry often involves the incorporation of the pigment into polymeric materials, such as paints and polyolefins. In this regard the durability of the pigmented system is quite important, since titanium dioxide can cause the thermal and photocatalytic degradation of the polymers, e.g. through the so-called 'chalking' process. Surface treatments have some effect in reducing this activity depending upon its type with the anatase form being more photoactive than the rutile.[17-23]

The current method for the evaluation of the durability of pigmented polymer materials depends on natural or accelerated weathering, which tends to be time-consuming and tedious in either case. From the mechanism described above, it appears that the photoactivity of the pigments is directly related to the photodegradation of polymers, hence some simple, fast alternative methods for the evaluation of polymer durability have been proposed and used. These include, for example, acetone formation in the photooxidation of 2-propanol,[24] voltaic effects and surface voltage measurements[25] and the electrophotographic and photodielectric microwave measurements discussed above.[12,13]

In this paper, the latter two methods have been used to study the effect of doping various transition metal ions into the crystal lattice of the rutile form of titanium dioxide over the concentration range 50 to 200 ppm. This is carried out by hydrolysis of titanium (IV) chloride in aqueous medium and simultaneous co-precipitation of the dopand ions as the hydroxide. The pigment is then fired at 1000°C to convert the anatase form to the rutile form and the ions into the highest oxidation state.[25] The results on both photoconductivity and photodielectric microwave absorption are consistent and show definite changes and trends which are discussed in terms of the ions acting as traps for photogenerated holes.

2 EXPERIMENTAL

2.1 Material preparation

Titanium (IV) chloride, obtained from Aldrich Chemical Company, UK in 'Analar' form, was hydrolysed in double-distilled water together with standard, quantitative amounts of dopant solution in the chloride form. After boiling for 30 min the precipitates were filtered and thoroughly washed with double-distilled water and then dried at 90°C in an oven. The samples were then placed in a furnace and calcined in air at 1000–1020°C for 1 h. The powder was then ground when cool and sifted through a 53-micron sieve to remove any coarse powder and produce a pigment with a consistent particle size. Analysis of the pigments by atomic absorption spectroscopy indicated the concentrations of the metal ions to be within ±10%.

2.2 Photoconductivity measurements

Solvent-cast films were prepared from pigment dispersions (40% w/w) of poly(vinyl carbazole) (PVK) (Luvican M170, BASF Ltd, Manchester, UK) at 5% w/v in dichloromethane, using a 50 μm K-bar and an impression bed. The substrate for the cast film was aluminised Melinex (Camvac Ltd, Thetford, UK) and this was previously coated, using a 5 μm K-bar, with a thin layer of vinyl chloride/maleic anhydride copolymer (VMCA) (1% w/v in acetone) obtained from Aldrich Chemical Company Ltd, Gillingham, UK.

To aid the dispersion of the pigments in the polymer solutions, glass beads (2·5–4·5 mm) were added and the suspensions were mechanically shaken in a flask shaker at the maximum speed for 0·5 h. The coated films were then air-dried for more than 24 h.

The dried films were mounted on the electrophotographic recorder (for construction and operation of this instrument, see Refs 11–13), and examined under positive charging. The photodischarge of the films was carried out using a mercury vapour lamp.

2.3 Microwave dielectric measurements

The instrument 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 g) were evenly distributed over a Perspex holder, and placed into the 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 (power 24V 250W).

3 RESULTS AND DISCUSSION

3.1 Photoconductivity measurements

The conductivity of a material is expressed as:

$$\sigma = \mathrm{e}(n\mu_n + p\mu_p) \tag{1}$$

where e is the electron charge, n and p are the densities, i.e. number per unit volume, of free electrons and holes, and μ_n and μ_p are the mobilities of the electrons and holes respectively.[1–4]

In a homogeneous crystalline material, the numbers of electrons and holes are assumed to be uniform throughout the material, and the photoconductivity arises when the material absorbs radiation and increases the values of n and p. Hence,

$$\delta\sigma = \mathrm{e}(\delta n\mu_n + \delta p\mu_p) \tag{2}$$

In a non-homogeneous material, the numbers of electrons and holes may not be uniform, and the photoconductivity may result from a secondary mechanism, involving a reduction in the resistance of the barrier in the material by the radiation used. and

$$\delta\sigma = \mathrm{e}(\delta n\mu^*_{\mathrm{b}n} + \delta p\mu^*_{\mathrm{b}p}) \tag{3}$$

where μ^*_{b} is known as the effective mobility.

It is assumed that the conductivity is dominated by one of the carriers, so that the contribution of the other can be neglected and that the material remains neutral during the photoconductivity process without a significant build-up of space charge in the material. When light falls on to a photoconductor, f electron-hole pairs are created per second per unit volume; thus

$$\delta\sigma = f\mathrm{e}(\mu_n\tau_n + \mu_p\tau_p) \tag{4}$$

where $f\tau_n = \delta n$ and $f\tau_p = \delta p$.

In the photoconductivity studies, the pigment is embedded in a polymer matrix—poly(vinylcarbazole) (PVK). When light falls on to the pigmented PVK film, the pigment can generate electron-hole pairs. PVK is a well known p-type photoconductor and its transport mechanism has been reported to involve a hole-hopping process. Electrostatic charges are deposited onto the surface of the pigmented films and these are neutralised by photogenerated carriers from the pigments and the PVK matrix. The exact mechanism of charge transport in pigmented PVK is still under investigation, but it is proposed that the PVK provides the majority of carriers, i.e. holes, and the pigment acts as an imperfection within the matrix, possibly as a trap, and this will delay the movement of the holes. However, the photoactivity of the pigment will be dictated by the speed at which the trapped holes are released, i.e. the higher the releasing speed, which will result in a higher photoresponse of the pigmented films, the lower the photoactivity of the pigments. Thus, the photoresponse of the pigmented films is an indirect measurement of the photoactivity of the pigments.

PVK films containing 40% w/w of the transition-metal-doped rutile pigments were positively charged for 10 s, and then photodischarged using UV light.[11-13] The photoresponse was characterised by the time taken to photodischarge the voltage to half of its initial value, called the half-life time of photodischarging. Table 1 shows the initial voltages that

TABLE 1
Initial Voltages of Pigmented Films with Different Concentrations of Various Dopants

Dopant	*Initial voltage (V)*		
	50 ppm	*100 ppm*	*200 ppm*
No dopant	7 2	7·2	7·2
Ni	6·8	10·3	9·8
Co	6·3	9·6	13·8
Fe	5·3	14·0	8·8
Pb	11·3	12·9	15·5
Cu	13·1	12·4	14·1
V	7·7	12·0	18·9
Mo	10·5	8·9	11·2

were retained before illumination on the surfaces of the pigmented films, which have concentrations of the various dopants of 50, 100 and 200 ppm. The initial surface voltage retained is seen to vary with the type of dopant, although there is no consistent trend, apart from an overall increase with increasing concentration. These results are consistent with those of other workers[25] who showed a similar effect, using different equipment, that was attributed to a decrease in pigment photoactivity. The influence of various dopants on the half-life time of photodischarging compared to that of the undoped control pigment is shown by comparing the data in Table 2. The data are also plotted graphically in Fig. 1 for easier comparison of the trends.

It is seen that, compared with the film containing the undoped pigment, those with the doped pigment showed a faster photoresponse. When doped with Mo, the pigmented film exhibited the shortest half-life, i.e. the fastest photoresponse. From the results, it can also be seen that

TABLE 2
Influence of Various Concentrations of Dopants on the Half-Life Time (s) of Photodischarging of Pigmented PVK Films

Dopant	*Half-life time (s)*		
	50 ppm	*100 ppm*	*200 ppm*
No dopant	3·41	3·41	3·41
Ni	3·34	1·88	1·77
Co	3·32	2·02	1·93
Fe	2·73	1·90	1·77
Pb	2·33	1·88	1·80
Cu	2·29	1·82	1·79
V	2·04	1·81	1·83
Mo	1·85	1·58	1·72

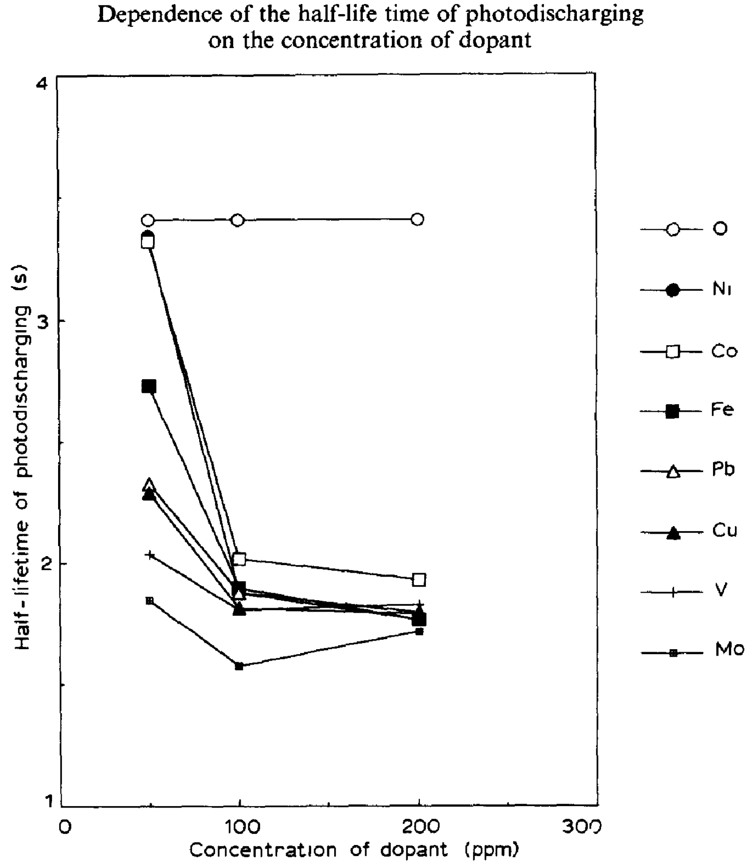


Fig. 1. Half-life of photodecay (s) discharge for rutile pigmented PVK films (40% w/w) versus concentration in ppm of (○) none, (●) Ni, (□) Co, (■) Fe, (Δ) Pb, (▲) Cu, (+) V and (⊞) Mo dopants.

the higher the concentration of the dopant, the lower is the half-life time, i.e. the faster is the photoresponse. However, the concentration effect is seen to be larger, for example, for Ni than Mo (Table 2) and follows the order in terms of enhanced photodecay:

$$\mathrm{Mo} > \mathrm{V} > \mathrm{Cu} > \mathrm{Pb} > \mathrm{Fe} > \mathrm{Co} > \mathrm{Ni}$$

It is also interesting to note that above 100 ppm concentration the values of the half-lives reach a plateau, i.e. they have reached a saturation level for the trapping sites. The above order is almost the same as that of the surface photovoltage (SPV) results presented by Luo and Gao.[25] The above results can be accounted for by the fact that the PVK is a hole transport medium and hence the transportation of electrons is limited to the pigment particles. For positive charging, carriers need to be formed

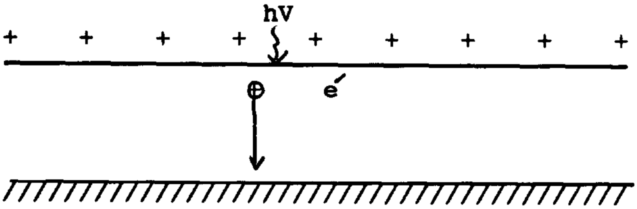


Fig. 2. Diagram for the photodischarging of positively charged films.

near the surface so that electrons can neutralise the charges, and the holes are then conducted through the bulk of the film as shown in Fig. 2.

As previously described, in the pigmented PVK films the PVK provides the majority of carriers, i.e. holes. Although the pigment can also generate hole and electron pairs when irradiated, it acts in the film as a hole trap. The high-energy photogenerated hole from the pigment can trap the electrons from the PVK and thus the speed of neutralisation of the positive charges decreases. In this case, the half-life times of photodischarging for the pigmented films are longer than that of the pure unpigmented polymer film. However, when the titanium dioxide pigment is doped with various dopants, it is suggested that the dopants substitute for the lattice titanium (IV), and the outer 3d or 4d electrons will behave as donors and thus effectively annihilate the high-energy photogenerated holes. Therefore, the holes from the pigment cannot trap the free electrons photogenerated from the PVK again, and will thus increase the rate of neutralisation of positive charges, and hence the photoresponse of the pigmented films will increase. When the difference in the atomic volumes of titanium and dopant becomes smaller, the overlap of the electronic clouds will become larger and this will result in a greater annihilation effect and thus a higher photoresponse and a shorter half-life time for the pigmented film.

3.2 Photodielectric measurements

Measurements on powders of ZnS, ZnO, or CdS types have shown that, if a photoconducting material is to be considered as the dielectric in a capacitor across an alternating field, then the radiation absorbed would increase the apparent dielectric constant of the capacitor. For a charged particle of negligible mass bound to a system of relatively high inertia the change in dielectric constant is:[1-4]

$$\delta\epsilon = \delta\epsilon_\infty + \frac{\delta\epsilon_0 - \delta\epsilon_\infty}{1 + \omega^2\tau^2} \tag{5}$$

The dielectric loss, expressed as the change in equivalent parallel conductance, is

$$\delta\gamma = \frac{(\delta\epsilon_0 - \delta\epsilon_\infty)\omega^2\tau}{A(1 + \omega^2\tau^2)} \tag{6}$$

where $\delta\epsilon_0$ and $\delta\epsilon_\infty$ are the changes in the dielectric constant at low and high frequencies, respectively, A is a constant, and τ is the relaxation time of the trapped electrons.

The dielectric measurements are carried out on the pigment samples alone, and the relative changes in the dielectric constant and the dielectric loss are related to the photoactivity of the pigment. Titanium dioxide is an n-type semiconductor, implying that electrons are the majority of carriers when conducting electricity. Thus, what will decrease the photoactivity of titanium dioxide will decrease the exhaustion of the free electrons and thus increase the photodielectric response. The dielectric constant can be indirectly measured from the cavity resonant frequency, and the dielectric loss from the Q factor of the resonant peak.

$$Q = \frac{\omega_{\min}}{\delta\omega} \tag{7}$$

where $\omega_{\min}$ is the resonant frequency, and $\delta\omega$ is the frequency difference at half the height of the resonant peak.

The resonant frequency is related to the interaction of the sample with the electric field component of the cavity mode. The resonant frequency value of the empty cavity is higher than when containing the Perspex holder, and both are higher than when containing the pigment samples (1·00 g). Thus, the absorption of the microwave energy in the latter case gives rise to a return frequency loss. From the undoped rutile to the Mo-

TABLE 3
Initial Resonant Frequency Shifts for Undoped and Doped Rutile Pigments

Dopant	*Resonant frequency shift (GHz)*		
	50 ppm	*100 ppm*	*200 ppm*
No dopant	0·0844	0·0844	0·0844
Ni	0·0884	0·0969	0·0965
Co	0·0893	0·0938	0·0971
Fe	0·0895	0·0980	0·1011
Pb	0·0937	0·0974	0·1012
Cu	0·0942	0·1055	0·1013
V	0·0957	0·0998	0 1027
Mo	0·0957	0·0972	0·1025

doped rutile, which is the same order as that for the photoconductivity measurements, the resonant frequency loss is seen to decrease. Therefore, the initial resonant frequency shift from that of the control increases, as shown by the data in Table 3 and the plot in Fig. 3. From this information, it can be seen that the initial resonant frequency shift increases with the concentration of the dopant. Since the resonant frequency loss is an indirect measurement of the dielectric constant of the material, this suggests that the doped rutile pigments are relatively less conductive than the undoped rutile. For the doped rutile pigments, the order of conductivity is:

$$\text{Mo} < \text{V} < \text{Cu} < \text{Pb} < \text{Fe} < \text{Co} < \text{Ni}$$

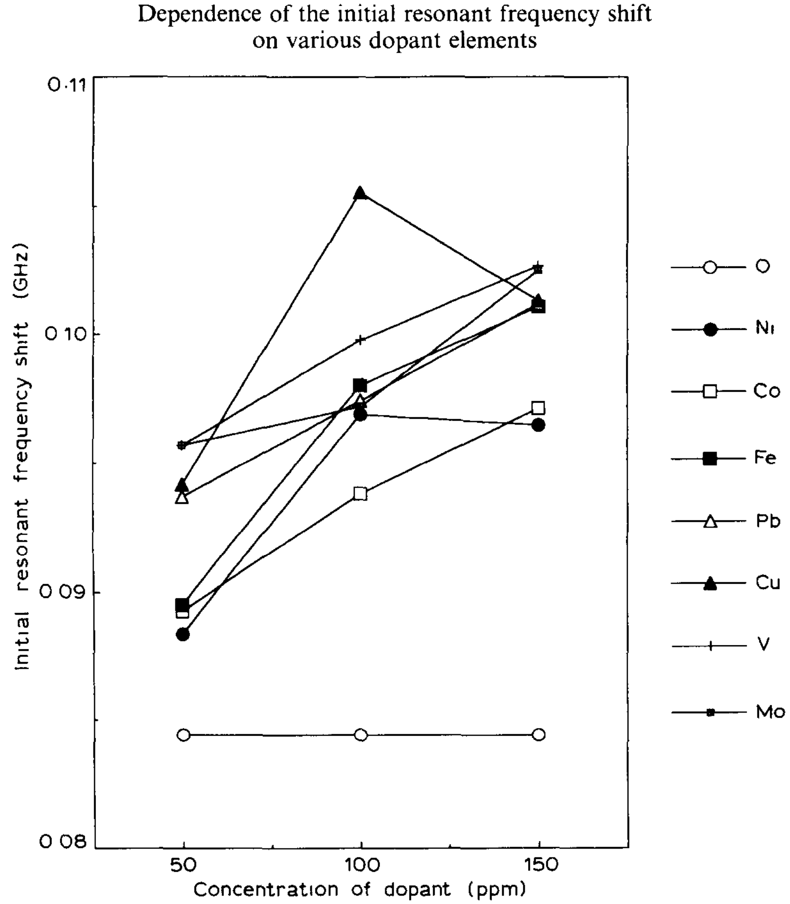
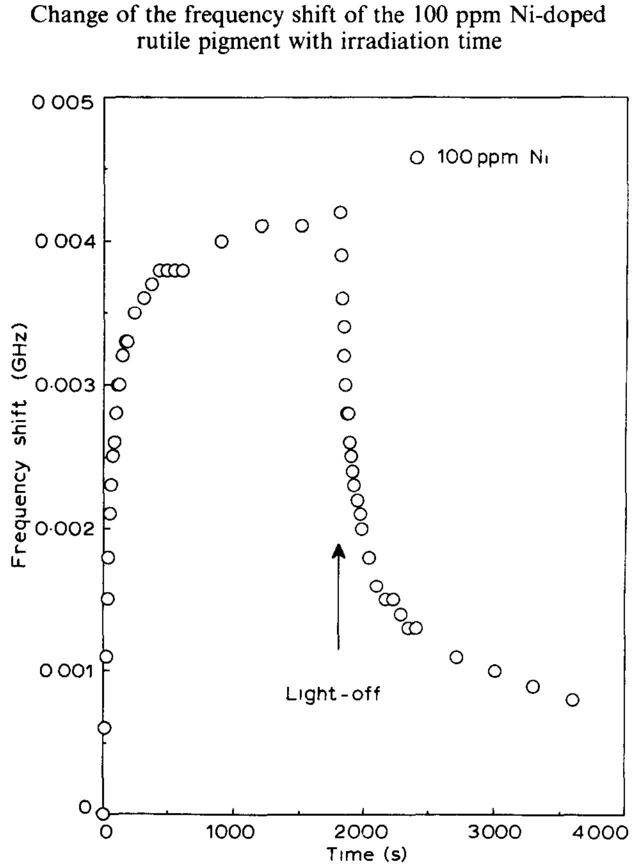


Fig. 3. Initial resonant frequency shift (GHz) for rutile pigments versus concentration in ppm of (○) none, (●) Ni, (□) Co, (■) Fe, (Δ) Pb, (▲) Cu, (+) V and (⊞) Mo dopants.

With an increase in the concentration of the dopant, the dielectric constant (Q-value), and thus the conductivity of the pigment, will decrease. The half-peak width of the resonant frequency absorption bands remained constant for different dopants, only the maximum changed.

When the pigment samples are irradiated in the cavity, the resonant frequency shifts towards higher frequencies, implying that the pigment is becoming more conductor-like. On termination of the light, the resonant frequency loss gradually returns to its original value, as shown in Fig. 4 for the Ni-doped rutile pigment. The latter indicates that the dielectric loss increases during steady-state irradiation, and then returns to its original state once the illumination is turned off.

The photodielectric half-life times and the dark-decay half-life times of



Change of the frequency shift of the 100 ppm Ni-doped rutile pigment with irradiation time

Fig. 4. Change in the resonant frequency shift for 100 ppm Ni doped rutile pigment during irradiation and after termination of light.

the various transition-metal-doped rutile pigments are compared in Figs 5 and 6 respectively. The photodielectric half-life time decreases when the rutile is doped, and has almost the same order for different dopants as that obtained in the photoconductivity measurements. Furthermore, when the concentration of the dopant increases, the photodielectric half-life time decreases. The dark-decay half-life time shows similar trends, but the data are more random.

Here, the annihilation of the high energy photogenerated holes by the 3d or 4d electrons of the dopants may play an important role. Titanium dioxide, as indicated above is an *n*-type semiconductor. Thus, the majority of the conducting carriers are electrons. When irradiated, the titanium

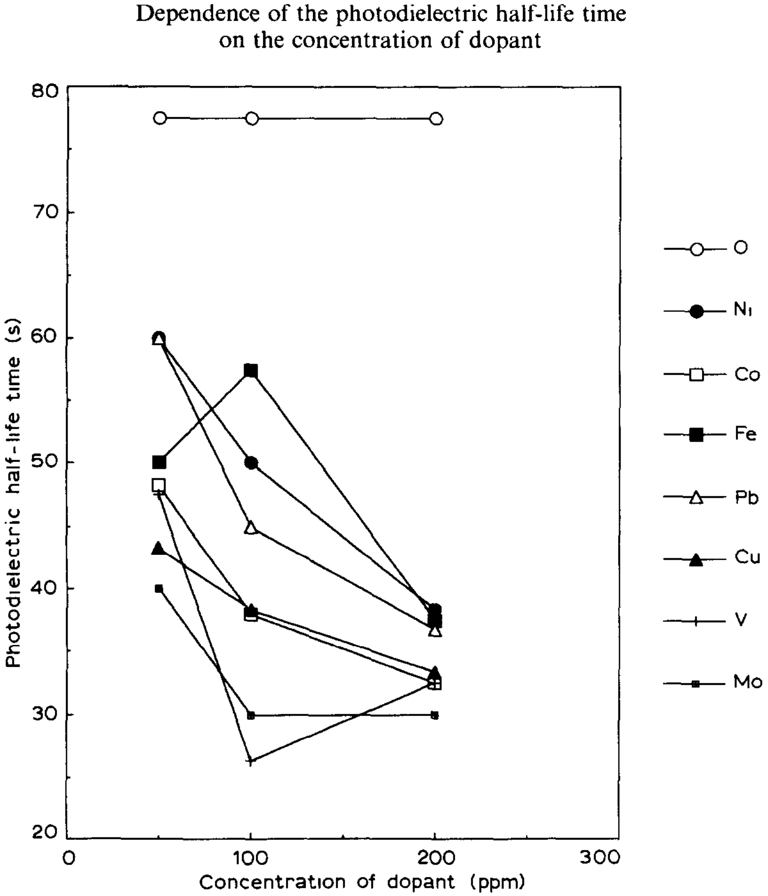


Fig. 5. Half-life of resonant frequency shift during irradiation (GHz) for rutile pigments versus concentration in ppm of (○) none, (●) Ni, (□) Co, (■) Fe, (Δ) Pb, (▲) Cu, (+) V and (⊞) Mo dopants.

dioxide can photogenerate holes and electrons on the one hand, but electrons can be captured by holes in the free state, imperfection sites, combination centres, or excited centres. If the pigment is doped with the transition metals which have polyvalent properties then the 3d or 4d electrons can annihilate the above holes. Therefore, the photodielectric response will increase. The same reason applies in the case of the dark-decay half-life time, but that of the undoped rutile is not the highest value, as shown in Fig. 6.

The above results are consistent with the surface photovoltage measurements (SPV) obtained earlier[25] which have been confirmed by photochemical measurements involving the photocatalytic conversion of isopropyl alcohol to acetone by the undoped or doped titanium dioxide pigments.[24]

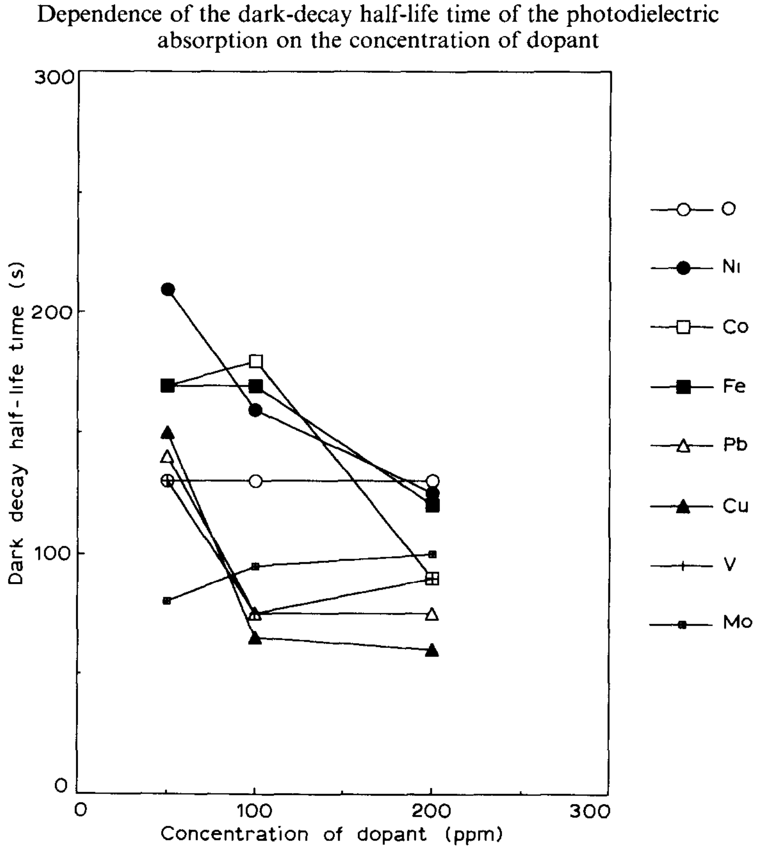


Fig. 6. Half-life of resonant frequency shift dark decay after irradiation (GHz) for rutile pigments versus concentration in ppm of (○) none, (●) Ni, (□) Co, (■) Fe, (Δ) Pb, (▲) Cu, (+) V and (⊞) Mo dopants.

4 CONCLUSION

The photoactivity of rutile titanium dioxide may be reduced by doping it with certain transition metal ions. The dopant substitutes for the lattice titanium (IV) and this results in a greater annihilation of the higher energy photogenerated holes in the pigment by the 3d or 4d electrons of the dopants, which act as donors. Therefore on doping, the photoresponses of the pigments are enhanced and the photoactivity of the pigment is decreased. Here, the recombination process is achieved by the impurity levels in the forbidden band of the titanium dioxide polycrystal introduced by doping. Correlation plots of the photoconductive and photodielectric responses with the atomic volumes and radii[26] of the dopants were found not to be linear. This may well be associated with the fact that the ions are present in mixed degrees of oxidation states, not all being present in the titanium dioxide crystal lattice. Indeed, it is reasonable to assume that some may well be on the surface. The form of the dopant is also crucial, since as in the photographic process for silver halides, the electron donating or accepting characteristics of the silver and developers will depend on their state, as well as the environment.[27] The photoconductivity and photodielectric measurements are therefore shown to be two sensitive and convenient techniques useful for the evaluation of the photoactivity of photoactive materials, and these in turn can provide valuable information on the durability of the pigment system. Future work will concentrate on modifying and perfecting the sample and measurement technique for quantitative analysis as well as detailed photoactivity studies.

ACKNOWLEDGEMENT

The authors wish to thank Ms Y. S. Chow, Mr A. D. Haigh and Dr R. Janes for their kind and helpful discussions with regard to the work described here.

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