FTIR Spectroscopy Studies of Photochemical and Thermal Processes on Offset Lithographic Printing Plates

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Abstract

Fourier Transform Infrared (FTIR) spectroscopy was used to study photochemical and thermal processes that take place during and after irradiation, and post-treatment, of lithographic printing plates. This technique was used both in Transmission as well as in Specular Reflectance mode. The processes studied included: a) Monitoring free radical photopolymerization of acrylate oligomers and monomers; b) Post-cure of the plates by baking at temperatures between 300°F (149°C) and 500°F (260°C); c) Following the photodecomposition of diazo molecules on commercial plate substrates. It has been possible to determine the induction period before polymerization when radical scavengers are present in the formulation. The implication of the results on the microstructure of the network is also discussed. Attempts were made to correlate some of these observations, such as the degree of polymerization (D.P.) and the mole-cular structure and physical properties of the monomer-oligomers used, with the performance of the plates, in particular with the resolution and the length of run on a commercial printing press.

Introduction

Lithographic plates are one of the main components in an off-set printing system.[1] The polymeric pattern photogenerated on the plate surface interacts directly with the ink, carrying it to a resilient roll, and this roll transfers the ink to the paper. The photoprocesses responsible for the formation of the polymeric pattern are similar to, and classified like, resist technology.[2] The printing pattern on negative working plates is the result of a considerable decrease in solubility generated by a light-induced dissociation or photo-induced cross-linking process,[3] while in positive working plates the light is responsible for an increase in solubility in the exposed areas by a photochemical-induced process.[4] The present work was concentrated on negative working plates.

Most negative plates use a surface modified aluminum sheet as substrate, on top of which is layered a photosensitive coating. This coating is made of a complex mixture of polymers (called binders), photosensitive materials, dyes or pigments, and monomers-oligomers or macromolecules containing polymerizable groups. In most cases the photosensitive materials are diazonium salts,[5] commonly in the form of a polyelectrolyte, which are photodissociated by UV light and result in a non-ionic polymer. This process changes the solubility of the original material and this is the basis for what is called a "diazo" plate. Other plates, besides having the diazonium salt, also contain acrylate based monomers-oligomers or functionalized polymers, which can undergo either polymerization or photo-induced cross-linking when a photoinitiator is present. As a result, a tough network (or cross-linked polymer) structure is formed in the exposed areas. In this case the plate is called a "diazo-photopolymer" plate. The final characteristics of the plate, as well as its performance on press, are very much dependent on the rate and efficiency of the photoprocesses that take place upon exposure. Therefore, it is important to determine the rate and degree of polymerization when monomers-oligomers are present, the rate and extent of the photodecomposition of diazonium salts, and analyze chemical and photochemical events that take place in the photocoat after irradiation.[6]

This report describes the use of transmission and Reflectance Fourier Transform Infrared (Re-FTIR) spectro-scopy to study such processes in "diazo-photopolymer" based plates. This technique was also used to determine the effect of baking lithographic plates to temperatures between 300 and 500°F (149 - 260°C), before and after irradiation. The usefulness of this technique in studying such systems was demonstrated when the role of some components in the formulation was determined, and the correlation between the influence of the component's photochemical behavior and the rate and degree of polymerization was also established.

Experimental

Materials

The formulations used for both transmission and reflectance experiments contained a polymer binder mixture, consisting of a thermoplastic polyurethane (from B.F. Goodrich, USA) and an acrylated epoxy polymer (from Echo Resins, USA), multifunctional acrylate monomers (from Sartomer, USA), a benzoin-type photoinitiator (from Ciba-

Geigy, USA), a co-initiator (sensitizer), a diazonium polymeric resin (from PCAS, France), and dyes and pigments, mainly for visible imaging. Some experiments utilized a phosphine oxide based photoinitiator (from BASF), plus propoxythioxanthone (PTX, available from Biddle Sawyer, USA), and benzanthrone (from Aldrich). The organic solvents used consisted of a mixture of glycol ethers. The total percentage of solids was about 4%.

Sample Preparation

For the transmission experiments a few drops of the solution was homogeneously spread on the surface of a sodium chloride window, and dried at 70°C for about 4 minutes. The thickness of the film formed was measured to be about 2 micron.[7] For the reflectance experiments the aluminum substrate was first coated with the photosensitive solution using a # 9 - 10 stainless steel coating rod. The plate was then dried in a lab drying oven for about 4 minutes at 70°C. The final thickness of the dried coating was measured to be around 0.500 micron.[7].The reflectance FTIR measurements were made on rectangular samples (2 × 3 inches), cut directly from the dried plate.

Radiation Source and Exposure Conditions

The plate samples were exposed either under vacuum (p ~ 100 torr) or in air, in a Teaneck Graphics exposure unit, equipped with an 8.0 kW Multi-Spectrum (MS) bulb, model L-1282, from Olec Corp (Irvine, CA). The emission intensity from this bulb is almost flat between 340 to 450 nm, except for some larger intensity spikes at approximately 405 and 418 nm. The exposure time was controlled by a light intensity integrator (model Olix AI-975 SC, also from Olec), and it was measured in "units". The number of "units" is very close to the number of seconds of exposure time, typically within 2 seconds for exposure times below 30 "units". The exposure time was appropriately changed depending on the experiment performed. For the transmission measurements the coated sodium chloride windows were first placed on a standard IR spectrometry metal holder, the holder was subsequently placed on top of the glass window of the exposure unit, and irradiated in the atmosphere. The total power output below 400 nm was measured to be about 125 mW. cm^{-2}, and seems to oscilate by approximately 3% during different exposures.

Baking Procedure

A resistance heated, convection oven was utilized for the baking experiments. The samples were placed on a support Aluminum plate (008 × 20 × 24 inches), and moved through the oven by a conveyor belt at an speed of approximately 30 inches per minute. The support plate used had always the same dimensions, including thickness, tomaintain similar heat absorption-reflectance characteristics on separate experiments and avoid large fluctuations on the surface temperature. Experiments were performed at 3000F (149°C), 400°F (204°C) and 500°F (260°C). These temperatures were measured at the Al support plate by heat sensitive plastic strips (from Cole-Parmer, Niles, IL), accurate to at least 5%. The residence time of the samples inside the oven was about 1.5 minutes.

Plate Development

Anitec's SP (subtractive plate) developer was used for all the plates tested. Typically 10 strokes were performed in the main (longer) direction of the plate, plus 10 more in the perpendicular direction, and, finally, 10 more strokes in the original direction. After extensive rinsing with water, the plates were dried at 70°C for 2 minutes in a lab drying oven.

Spectroscopic Measurement

A full report describing the experimental techniques developed, as well as applications of these techniques to problems concerning lithographic printing plates, is still to be published. In brief, a Magna-550 FTIR spectrometer from Nicolet Corp. (Madison, WI) was used at resolutions between 1 and 4 cm^{-1}, depending on the experiment . Sixty four to one hundred twenty eight scans were performed for each spectrum in the range between 4000 - 600 cm^{-1}. A specular reflectance accessory designed by Pike Technologies (Madison, WI) was utilized to analyze directly the plates. The plate support in this accessory had three guiding screws to help the reproducible positioning of the lithoplate samples. For the transmission experiments a single coated sodium chloride window was placed on a standard metallic IR spectroscopy holder, and this holder was positioned perpendicular to the IR beam.

The measurements followed the same basic technique originally developed by Collins and Constanza[8] and extensively improved by Decker in recent years.[9] The acrylic band at about 810 cm^{-1} was used to measure the relative amount of acrylic groups in the system, for both reflectance and transmission experiments. The **% C = C** (also taken as the Degree of Polymerization, **D.P.**) was determined as

$$[\%\ C = C] = [A_{bef.} - A_{aft.}]/A_{bef.} \qquad (1)$$

where $A_{bef.}$ is the area of the band measured before irradiation, and $A_{aft.}$ is the area measured after irradiation. From tests performed in other experiments, it has been determined that the area of the peak normally used as an internal standard, at around 1730 cm^{-1}, and which corresponds to the C = O bond, does not change significantly after irradiation. Therefore, no attempts were made to use this intensity fluctuation to correct the directly calculated % C = C, in the experiments performed so far.

Results and Discussion

Several experiments were performed using some acrylate-based plate formulations, including:

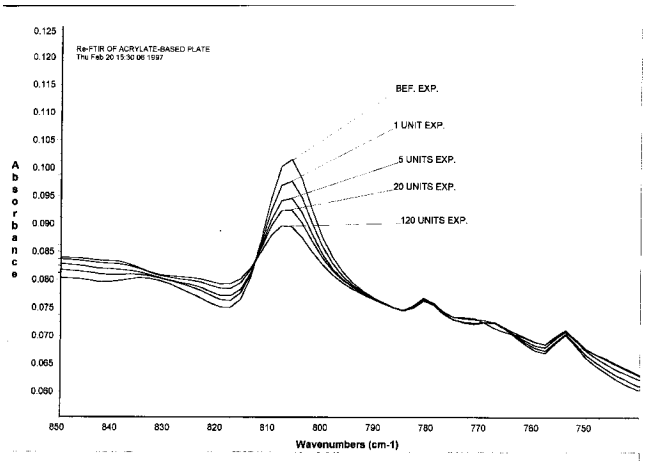

Figure 1 : Re-FTIR spectra showing the 810 cm-1 band of an acrylated-based plate sample submitted to a sequence of exposures.

Evolution of the Degree of Polymerization with Exposure Time

Figure 1 shows the spectra between 850 and 740 cm^{-1} of a plate sample made with the basic formulation, and which has been subjected to different exposure time. The % C = C was determined after each exposure and the results are plot in Figure 2 a. It is possible with these results to determine what the ideal exposure time for the plate should be. It is also quite apparent the effect a short exposure time (e. g., 10 units) would have in the polymer network. The D.P. corresponding to 10 units is lower than at 20 units exposure (38% compared to 44%) for samples irradiated under vacuum. This results in a much softer (lower D.P. and lower cross-linking density) network being formed and, normally, the consequence is lower length of run of the plate on press. Figure 2 b depicts the results of similar samples exposed in air. It clearly shows the effect of oxygen in the acrylic polymerization process. Since it is a free radical process, oxygen interferes, mainly with the propagation step,[10] and this is deleterious to the formation of the network.

The Role of Some of the Components in the Plate Formulation:

The usefulness of the Re-FTIR technique in understanding the role of some of the components of a plate formulation in printing plate characteristics, such as resolution, speed, post exposure visible image contrast, and even cosmetics, was also demonstrated. It has been observed, especially in acrylate based plates, that because of the high photo-sensitivity of some coatings, light-induced cross-

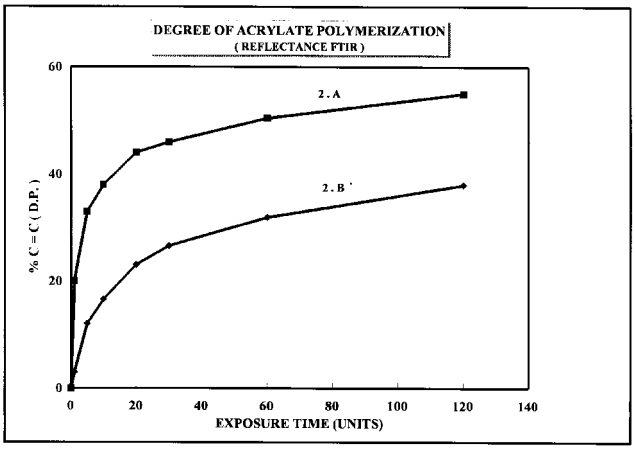

Figure 2. Evolution of the degree of polymerization (D.P.) of an acrylate network formed on lithoplate samples irradiated under vacuum (2.a) and in air (2.b), determined using Re-FTIR spectroscopy data.

linking processes may take place in areas under very low illumination levels. Depending on the type of monomer used and the final cross-linking density attained, pigments and dyes may be trapped inside the network. Therefore, they are not easily removed, upon development, from the areas where no polymerization should have taken place. The result is the presence of several spots, colored like the initial plate, in regions that should be clear. They are normally called "hot spots". This problem is also quite apparent in the borders of the film mask, used for the printing exposure, and in this case it is referred as "halation". It has been observed that the addition of benzanthrone into the formulation is able to basically eliminate the presence of "hot spots" and "halation" in acrylate plates.[11]

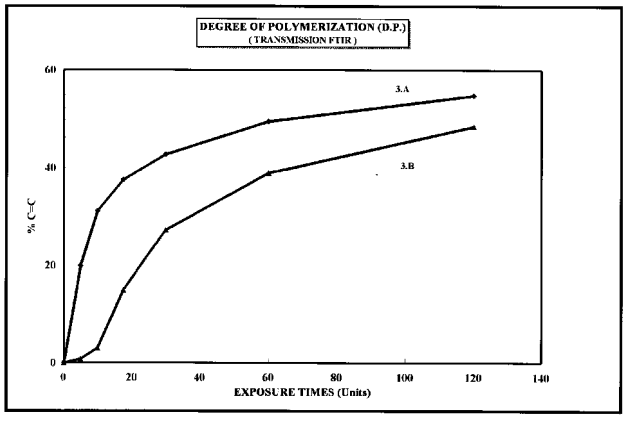

Figure 3 : Transmission FTIR spectra of coatings containing acrylate monomers-oligomers and using TPO/PTX as photoinitiator (3.a), and the same formulation after adding benzanthrone (3.b).

Benzanthrone is known to be a free radical generator[12] but apparently can also behave as a radical scavenger. This is

shown in Figure 3 where the D.P. is plotted against exposure time for a formulation containing the same basic components described before, except that the phosphine oxide and PTX were used as photoinitiators (3.a), and another formulation with about 0.04% of benzanthrone added (3.b). The latter clearly shows that in the beginning of the irradiation process benzanthrone is acting as a radical scaven-ger. Only after most of the benzanthrone is consumed, the photopolymerization proceeds at a higher rate, reaching a D.P. comparable (but still smaller) to the standard formula-tion. Although it seems most likely that benzanthrone is acting as a radical scavenger in the specific formulation and radiation conditions studied, it is also possible that it may be reacting photochemically with the triplet state of one the photoinitiators. To clear this point some flash photolysis work would be necessary.

The observations above seem to indicate a correlation between the rate of network formation and the cross-link density. When benzanthrone is not present the photopolymerization takes place at high rate and a relatively high cross-link density network is formed. The pigments (or dyes) trapped in this "tight cage" cannot be removed during development. When benzanthrone is added, the photopolymerization is slower, a large number of initiating species are formed and this results in a more open network. The pigments (or dyes) species are much easily removed from the coating medium with the developer. This photo "hypersensitivity" and high polymerization rate contribute to reducing considerably the resolution of the plate. The inverse relation-ship between the rate of photopolymerization and the resolution of the plate seems to hold true for plate formulations containing multifunctional acrylate monomers-oligomers, especially those with functionality greater than four.[13] The slight decrease in D.P. observed, and the apparently more open network formed, tend to decrease the length of run of the plate on press.

Baking Experiments:

Several experiments involving baking the plates at different temperatures were performed. These experiments were stimulated by field observations that an increase by almost ten times in the normal length of run has been observed in some acrylate-based plates, when baked to temperatures around 500°F (260°C). This study is directed towards the development of a methodology that could help the understanding of what happens, at the molecular level, during the irradiation, baking, and development stages of plate processing. The following describe the observations.

Baking + Development (No Light Exposure):

This experiment consisted of first baking different samples to 300, 400 and 500°F, and then developing them with a standard subtracting developer. The FTIR spectrum of each sample was scanned before and after the baking procedure, in order to determine both the percentage of monomer vaporized by the heating, and the relative amount that had undergone thermal polymerization. A new spectrum was also taken after development of each sample, in order to determine the amount of monomer removed during the development stage. The following guidelines were used in the interpretation of the data : (i) The 1730 cm^{-1} absorption band, corresponding to the C = O bond of the acrylate monomer, was used as the internal standard, and as the indicator of monomer concentration in the plate coating. An increase (normally small) in the intensity of the C = O band ($I_{C=O}$) is associated with film shrinkage due to the photopolymerization. A decrease in $I_{C=O}$ is associated with monomer removal from the coating, either by vaporization (during the baking stage) or physical removal (after development). (ii) The 810 cm^{-1} absorption band, related to the C = C bond of the acrylic group, was used mostly to diagnostic the polymerization process, either thermal or photo-induced. A decrease in $I_{C=C}$ is related to an increase in the D.P. However, if polymerization is not expected to occur in the system, the intensity $I_{C=C}$ is also related to the concentration of the monomer. In some experiments, changes in $I_{C=C}$ were used as a measurement of monomer removal.

Since during the baking procedure there is a possibility of some processes occurring simultaneously, especially vaporization and thermally-induced polymerization, the degree of thermal polymerization, **% POLY**, was calculated using the following relationship:

$$\% \text{ POLY} = \Delta (\% \text{ C=C}) - \Delta (\% \text{ C=O})$$

where Δ **(% C = C)** represents the percentage decrease in the amount of C = C bonds, due to either thermal polymerization or evaporation, while Δ **(% C = O)** is related only to the percentage of monomers evaporated during the baking process. As suggested above, the two main observations in these baking plus development experiments were:

Monomer Vaporization:

The percentage of monomer vaporization was determined by measuring the decrease in $I_{C=O}$, or :

$$\% \text{ Vaporization} = D\,I_{C=O\ (1730\ cm^{-1})} \qquad (3)$$

Actually, this peak intensity measurement was not just the peak height, but rather the absorption band area, $A_{C=O}$. Table 1 below (2nd column) displays the percentage average over three samples of monomer vaporized from the baking experiments at 300, 400 and 500F.

Table 1. Effect of Baking and Developing Acrylate-Base Plates

Bak. T (oF)	Evap. (%)	T-Poly (%)	Rem. Dev.(%)	Left (%)
300.00	1.30	5.00	91.00	2.70
400.00	33.00	15.40	42.00	9.60
500.00	39.40	29.60	6.00	25.00

These results are quite expected, with higher temperatures corresponding to higher percentage of vaporization because of the direct relationship between vapor pressure and temperature.

Thermal-Induced Polymerization:

The degree of thermal induced polymerization was determinedby measuring both the percentage of disappearance of the C = C bonds (changes in A c = c) and the disappearance of C = O bonds (changes in the A c = o). As discussed above, the D.P of thermal-induced polymerization was determine using:

$$D.P. = \%\,\Delta\, I_{C=O\ (810\ cm\text{-}1)} \%\,\Delta\, I_{C=O\ (1730\ cm\text{-}1)} \quad (4)$$

In the expression above the decrease in $I_{c=c\ (810\ cm\text{-}l)}$ corresponds to the disappearance of acrylic groups (both by vaporization and by thermally-induced polymerization) while a decrease in $I_{C=O\ (1730\ cm\text{-}l)}$ corresponds to the amount of monomer lost by vaporization alone. Table 1 (3rd column) presents the percentage of monomers thermally polymerized 300, 400 and 500°F.

Monomer Removal by Development

After baking at 300, 400 or 500°F, the plates were developed using a subtractive developer. Two independent measurements were performed to evaluate the percentage of monomer removed by the development. First, the total percentage of monomers vaporized and removed by development was determined from the changes in intensity of the C = O band at 1730 cm^{-1}. Since the percentage of monomers vaporized is already known the amount removed by development could be calculated. An alternative way to determine the percentage of monomer removed by the development was to measure the intensity of the acrylic related band at 810^{-1} cm. The overall decrease in the acrylic band intensity is related to the amount of monomer vaporized by the baking, plus the monomer thermally polymerized, and the percentage of monomer removed by the development. Knowing the amount vaporized and the amount thermally polymerized the amount removed by development could also be calculated. The results show a good match between the two calculations (l to 2 % difference) and validate the assumptions about the changes in $I_{C=C}$ and $I_{C=O}$, and their correlation with polymerization and monomer removal.

With this information it is now possible to have a full mass balance of the monomer throughout the processes that the plate has undergone for the samples baked at all three different temperatures. For baking at 300°F, 1.2% of the monomer evaporates, about 4% thermally polymerize, 91.6% is removed by the development, and 3.2% is left "trapped" inside the remaining plate coating. At 400°F, 32.7% evaporates, 15.6% thermally polymerizes, about 42% is removed by development, and 9.7% is left "trapped" in the plate. At 500°F, 36.2% evaporates, 32.4% thermally polymerizes, 6.2% are removed by development, and 25.2% is left in the plate.

The main conclusions form these observations are discussed below. The amount of monomer evaporated is directly proportional to the temperature, because of the relationship between temperature and vapor pressure.

The amount of monomer thermally polymerized (D.P.) is also proportional to the temperature. An increase in temperature tends to soften the polymer binders and increases the thermal agitation of monomers and reactive species in the formulation. Both these factors increase the collision rate between coating components and this increases reaction probability. Besides this it is expected that heating the plate would tend to decrease the amount of oxygen dissolved in the coating, and also decrease the diffusion rate of oxygen through the coating Finally it is possible that the polymerization inhibitor(s) may be partially decomposed during the baking at high temperatures, and this would facilitate the rate of propagation of the polymerization (networking).

Removal of monomer by the development stage is inversely proportional to the temperature. It can also be said that the percentage of monomer removed is inversely proportional to the degree of polymerization of the network. This is expected since the diffusion of species through a network is related to the cross-linking density. In this particular case, cross-linking is proportional to the D.P.

The amount of monomer left in the coating is proportional to the temperature. This residual amount of monomer is a result of an intricate balance of different effects. For example, an increase in temperature would tend to decrease the monomer concentration (because of vaporization), while at the same time "tightening" the monomer to the plate (by the formation of a network through thermal polymerization). It is basically very difficult to predict what the outcome of these competing processes would be. Only experimental data could show the overall tendency.

Exposure + Development + Baking (300, 400, 500°F)

These experiments closely resemble a common practice on plate processing in the printing industry. Three different sets of plate samples were first irradiated to 5, 12, or 17.5 units, respectively. They were all developed with SP developer, and three smaller sets of each group were baked to 300, 400 and 550°F. The reflectance FTIR techniques previously described were utilized to determine the percentage of monomers photopolymerized by the initial exposure, the relative amount removed after the development, the percentage thermally polymerized after the baking, and the amount left unreacted on the plate. Table 2 displays the bulk of these results.

Table 2. Relationship Between the Irradiation Time, the D.P. of the Network Formed, and the Amount of Monomer Removed After Development of an Acrylate-Based Plate.

Sample	Exp.Time (Units)	% C = C (AVE.)	Δ A dev.(%, Ave.)	Mon. Left %
A1	17.5	50	- 12.6	37.5
B1	12	44.3	- 17.6	38
C1	5	36.8	-26.1	37.1

The last column represents the relative amount of monomers remaining in the plate up to and just before the baking step. As mentioned above, after each irradiation plus development procedure smaller sets were baked to 300 400 and 500°F. Table 3 displays the results after this last baking stage.

Table 3. The Effect of Baking Acrylate-Based Plate Samples to 300, 400 and 500°F, After Irradiation at 5, 12, 17.5 Units with the MS-Bulb Under Vacuum

Sample	Irrad. Time (Units)	Bak. T (o F)	D T-Poly (%)
D1	5.00	300.00	-0.90
E1	12.00	300.00	0.40
F1	17.50	300.00	0.30
D2	5.00	400.00	0.90
E2	12.00	400.00	1.30
F2	17.50	400.00	2.30
D3	5.00	500.00	7.80
E3	12.00	500.00	8.50
F3	17.50	500.00	7.00

The main points taken from these results can be summarized as follows. The amount of monomer removed by development is inversely proportional to the degree of polymerization of the formed network (in other words, to the irradiation time); the higher the D.P. (and the cross-linking density) the lower the amount of monomer removed. This is intuitively expected and has been discussed in the pure baking experiments.

After irradiation time in the 5.0 to 17.5 units range, and subsequent development, the amount of unreacted monomer left in the plate is basically constant, and equal to about 37.5 %. This seems to indicate that there is a D.P. value (close to, or slightly below 36% for our photosensitive system) beyond which the cross-linking density is so high that physical removal of monomers by development is independent of further polymerization.

After baking at 400 and 500°F some thermal polymerization could be observed (about 2 and 8%, respectively), while not much change was observed at 300°F. This is in agreement with what has been observed before, with higher temperatures corresponding to the higher degree of thermal polymerization. However, it is remarkable that an increase of just about 20 % in the normal degree of polymerization observed for baking at 500°F, plus partial removal of unreacted monomers, could account for the considerable increase in length of run observed. It is possible, and probable, that other chemical and physical changes (involving the binders) may be also taking place in the coating, simultaneously with the thermal polymerization of the monomers.

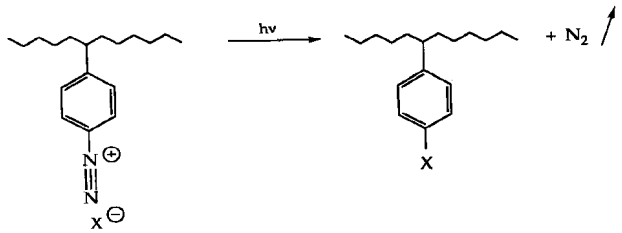

Figure 4 : Photodecomposition of a diazo resin under UV irradiation. Shown is one of the possible reaction paths.

Rate of Diazo Photodecomposition

As mentioned before, diazonium salts, in the form of polymeric resins, are one of the major components of most negative plates. It apparently plays several roles in the plate formulation, including participating in the visible imaging contrast after exposure, and being responsible for the drastic decrease in local solubility to the (polar) developer medium, through its photo-decomposition and change into a non-ionic polymer (Figure 4). The thermal and photo properties of the diazo resins are determined by several factors, including the counter ion of the polyelectrolyte, the type of substituent of the aromatic ring next to the azo group, molecular weight of the resin, to name a few. The final performance of the diazo is determined not only by the role that each one of these factors have on its characteristics, but also on subsequent reactions of molecular fragments, generated after the diazo decomposition, with other plate components. In attempting to understand better and quantify these effects, it is important to be able to measure the rate of diazo photo decomposition in a plate formulation and correlate these values with the plate parameters (resolution, apparent speed, percent dot, etc.).

Figure 5 displays the Reflectance FTIR spectra between 2000 and 2300 cm^{-1} of several commercially available plates. The figure clearly shows the absorption features corresponding to the $C \equiv N^+$ group of the diazo resins of each plate. Also shown is the absorption spectrum of one of the resins after irradiation for 5 units with the MS-bulb of our exposure unit. The spectra were analyzed and the absorption band areas of each resin used to calculate the relative rate of diazo photodecomposition using an equation analogous to (1).

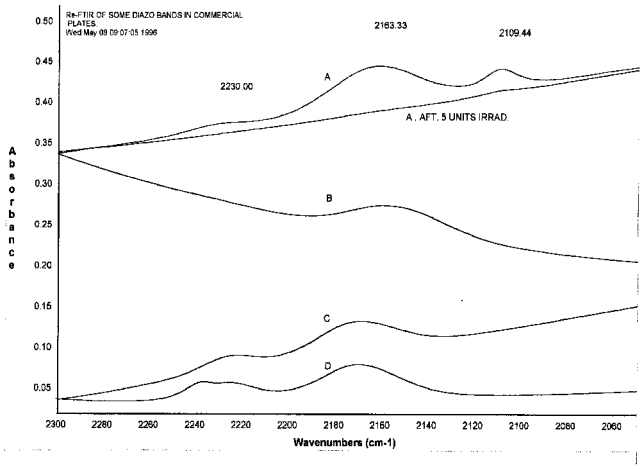

Figure 5 . Re-FTIR of commercial plate samples (A - D) showing diazonium salt bands. Also shown is the spectrum of one of the plates (A) after irradiation for 5 units.

Figure 6 displays the results. Although, as mentioned before, the diazo properties and performance in the plate depends on several factors besides its photodecomposition properties, it is interesting to remark that the fastest decomposing diazo is found in the plate with highest apparent speed.

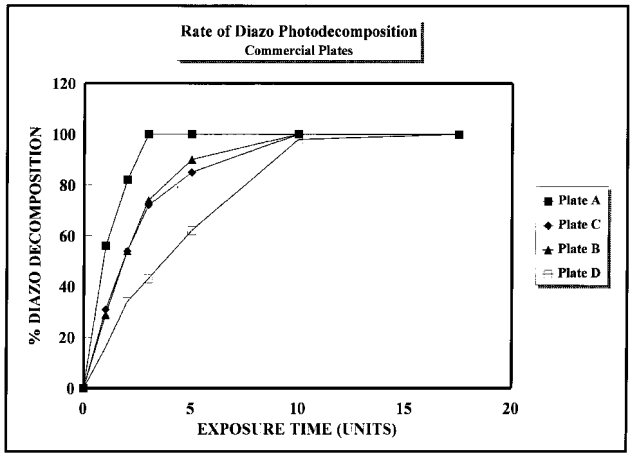

Figure 6. Relative rate of photodecomposition of diazonium salts present in four different commercial plates.

Final Remarks

The main goal of this paper was to present a useful, versatile and reliable method of analysis that could be utilized in the microscopic characterization of different types of coatings. A recent publication describes the use of Attenuated Total Reflectance (ATR) FTIR to study acrylate coating[14] polymerization. The present arrangement, using Specular Reflectance FTIR, may be advantageous in some applications, because it is operationally easier. The work described corresponds to applications where the scientific data gathered has enabled a great insight to be gained in the photochemical processes of interest to our business. It is also important to note the reflection techniques described, at this stage, are more semi-quantitative, since no curve fitting or detailed mathematical manipulation of the data was employed to correct properly for band shapes. Nevertheless, it is clear that the information acquired by these techniques can be extremely valuable in the design of new products.

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