Evaluation of Alkane Sulfonic Acid Catalysts and Derivatives for Curing Activity in a Melamine/Acrylic Polyol Coating Formulation Using Fourier Transform Infrared Spectroscopy

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INTRODUCTION

Alkane sulfonic acids and derivatives are a relatively new class of acid curing agents and, depending on their composition, can act as active or latent catalysts for curing melamine resin (reaction with the acrylic polyol added) based coatings for a variety of applications. They have the distinct feature of producing coatings for metal surfaces which provide good corrosion resistance, solvent resistance, hardness, and gloss at low catalyst loadings. These catalysts find applications in automotive clearcoats, basecoats, primers, and coatings for coils and cans as well as powder systems. Understanding the mechanism of catalysis and qualifying performance are critical parameters in the design of effective catalysts and making appropriate application selections.

Fourier transform infrared spectroscopy (FTIR) techniques provide a unique opportunity to study chemical changes[1-4] based on the complexity and specificity of the infrared spectrum. Major functional groups, whose changes are associated with reaction progress, have well defined wavenumber positions and shapes in the mid-IR spectral range. These characteristics can be exploited to provide detailed information on reaction kinetics, extent of completion, and in many cases mechanistic information. As the reaction proceeds, the system's properties change and the IR measurements can serve as a probe for these changes. Furthermore, IR measurements may be able to replace more laborious physical property determinations and thus serve as an efficient predictor. Literature examples include the work of C.-P. Yang and L.-T. Lee[5] on the cure of glycerin-terminated urethane prepolymers, Y.S. Yang and L.J. Lee[6] on the cure of unsaturated polyesters, C.A. Pryde[7] on imidization reactions, and D. Louden[8] on the acrylate cure in optical fiber coatings. In all cases, the studies were based on the selection of specific absorbances originating from functional groups involved in the chemical reaction. Disappearance and formation of species can thus be directly monitored.

The cure reaction of melamine-based systems has been extensively studied in the literature[9-15] as a result of its commercial relevance in industrial coatings applications.

FTIR measurements may be able to replace more laborious physical property determinations and thus serve as an efficient screening methodology in catalysis driven processes. This possibility was considered in evaluating alkane sulfonic acids catalyst performance to promote the cure of a melamine resin with acrylic polyols. The example chosen here is an evaluation of alkane sulfonic acid derivatives to measure catalytic efficiency of the cure reaction between hexamethoxymethylmelamine (HMMM) and an acrylic polyol. The IR measurements provided information on the extent of reaction, via monitoring the disappearance of the OH stretching mode at 3472 cm^{-1} associated with the acrylic polyol. This method may also be used to provide detailed information on reaction kinetics and insight into the cure mechanism. As the reaction proceeds, the coating's properties change and IR measurements can serve as a probe for these changes.

The studies have focused on understanding the crosslinking mechanism, kinetics, and the influence of reactants' structure. M. Lazzara[9] discussed techniques to measure degree of conversion. Among the techniques outlined were solid-state NMR, FTIR, and continuous monitoring of reaction volatiles. The effect of catalyst level, reaction temperature, and polyol structure was investigated. The FTIR technique had significant limitations due to the need to compare spectra acquired at variable temperature and the lack of experimental data to deconvolute the reaction effects from known temperature effects on the IR spectrum. Ohe and co-worker[10]

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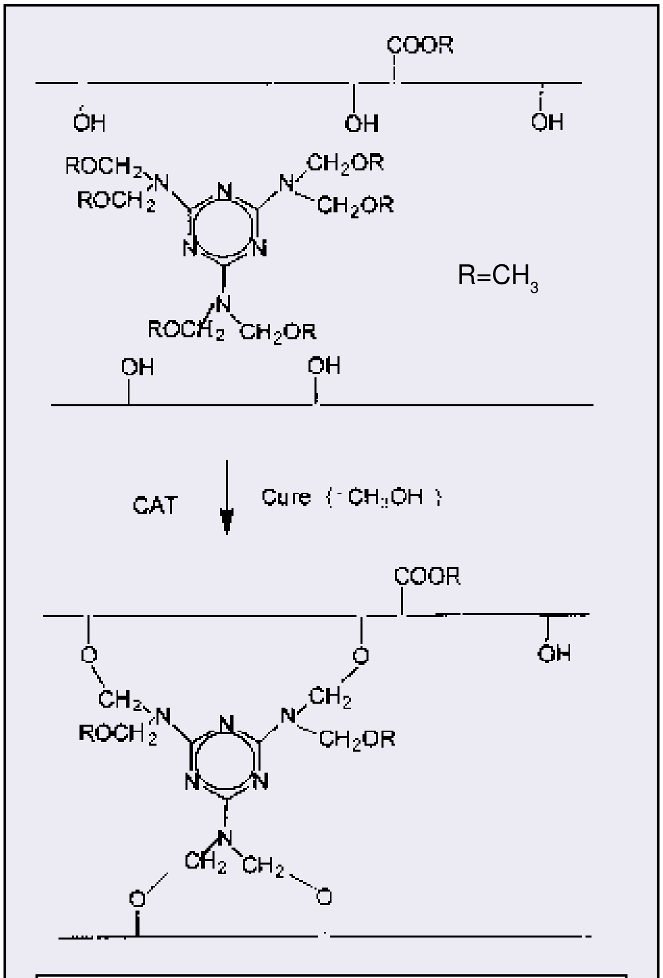

Figure 1—Cure reaction for HMMM with a polyol.

studied the kinetics of acid catalysis employing weak acid self catalysis to slow reaction rates. Both changes in the relative viscosity and IR absorbances associated with OH and OCH_3 groups were employed. The reaction pathways involved transetherification and self-condensation. Primary OH groups were found to react faster than secondary OH groups. At cure temperatures below 140°C and with primary OH groups, transetherification was the dominant pathway. Self-condensation occurred at higher temperatures or with secondary OH groups. The effect of the melamine crosslinker structure on the cure mechanism and coating properties is discussed by Blank[11] and Lee.[12] Yaseen[13] examined similar effects associated with the use of oligourethane diol rather than acrylic polyols. A detailed mechanistic and kinetic study of the melamine polyol reaction is found in the work of Zimmt and coworkers.[14] The rate of methanol evolution and gel formation (insoluble fraction) was utilized to provide kinetic data for two acrylic polyols reacting with melamine. Two sulfonic acids and their dimethyloxazolidine salts were used as catalysts. The rates of methanol evalution were found to be dependent on the concentration and nature of the catalysts and proportional to $[H^+]$ concentration. Gelation depended on the chemical structure of the polyol. Methanol evolution was not found to be dependent on the gel content or the glass transition temperature at cure temperatures of 120°C. The crosslinking reaction was also studied by Bauer and Budde.[15] The extent of cure was determined using the OH absorbance of the polyol. An expected rate increase was found with increasing the reaction temperature and the catalyst concentration, and the amount of methanol evolved decreased with increasing conversion. Among the catalysts utilized were acids of varying strength including para-toluenesulfonic acid (PTSA) and the isopropylamine and triethylamine salts of PTSA. These were found to reduce the cure rate as compared with the free acid.

This paper investigates the effect of the catalyst structure on the cure of hexamethoxymethylmelamine (HMMM) with an acrylic polyol. The catalysts used are alkane sulfonic acids and amine blocked derivatives. Some of these classes of catalysts have been previously mentioned in the literature,[14,15] but no systematic study of their effect was investigated. The structure of the reactants is invariant to enable the evaluation of only catalytic efficiency. FTIR is utilized as a fast and reliable methodology for catalysts comparison.

EXPERIMENTAL

Materials and Reagents

The following catalysts were employed in this study:

- methanesulfonic acid (MSA) from ATOFINA Chemicals, Inc.,
- para-toluenesulfonic acid (PTSA) from Aldrich,
- dodecyl benzenesulfonic acid (DDBSA) from Acros Organics,
- amine blocked alkanesulfonic acid (MCAT™1219S and MCAT™1300) from ATOFINA Chemicals, Inc.,
- amine blocked para-toluene sulfonic acid (BYK™ 460) from BYK-Chemie,
- amine blocked dodecylbenzenesulfonic acid (Nacure® 5543) from King Industries,
- a terpolymer of styrene with 2-hydroxyethylmethacrylate and methylmethacrylate (Joncryl™ 500) from SC Johnson Polymer, and
- hexamethoxymethylmelamine (HMMM) (Cymel® 303) from Cytec or Resimene® 547 from Solutia can be used.

Sample Preparation

The samples were prepared by mixing 70 parts acrylic polyol, with 30 parts HMMM and the catalyst (all at 0.02 mole/kg resin mixture). Samples for each catalyst system were deposited on aluminum foil covered glass slides. The films were thin enough to afford absorbances below IR saturation in the spectral region of interest. The samples were cured at 120°C for 0, 5, 10, 15, 20, 25, and 30 min in a forced air oven.

FTIR Measurements

A number of techniques are available for spectral acquisition in IR spectroscopy. For the purpose of this study, we have chosen grazing angle FTIR. Grazing angle FTIR[16-17] is a reflection/absorption technique characterized by high angles of incidence (85°). In a grazing angle experiment, the material is deposited as a thin film on a highly reflective metal surface. The incident IR beam that is reflected from the surface interacts with the film yielding an absorption spectrum. Spectra obtained using grazing angle FTIR spectroscopy resemble transmittance spectra (the technique is sometimes referred to as double pass transmittance).

The spectra were obtained on a Biorad 60A FTIR equipped with a grazing angle accessory. A DTGS detector was used, and 100 scans were co-added at 4 cm^{-1} resolution. Each spectrum was baselined, offset to a zero baseline value, normalized using the absorbance value at 3027 cm^{-1} (aromatic CH stretch), and further normalized to 1 for the sample prior to curing (time = 0 minutes). Normalizing the spectra eliminates the effect of varying sample thickness and permits effective comparison between samples. The normalized peak absorbance of the OH stretch (3400-3500 cm^{-1}) was then obtained and plotted against cure time to obtain a reaction profile for each catalyst. The choice of IR transition is similar to those in the work of Bauer and Budde.[15] Film thicknessess are estimated at 1-3 μm. Literature data has indicated that there is no dependence on thickness[15] for films of 25 μm. All IR measurements were performed at RT.

MEK Double Rub Test

The methyl ethyl ketone (MEK) double rub test is a solvent rub technique adapted from a standardized test (ASTM D 5402-93). It is used for assessing the resistance of an organic coating to MEK, and this reflects the chemical changes (crosslinking) occurring during the curing process. In our version of the test, the 7/8 in. head of a double sided 3/4 and 7/8 in. wrench is wrapped with a piece of cheese cloth. The cheese cloth is dipped into MEK just before the start and rubbed forward and backward over the coated surface. One forward and backward motion constitutes one double rub. The cheesecloth is dipped into MEK every 25 double rubs until the coating layer gets damaged. The uncertainly of the results is +/- 25 double rubs, and we consider a resistance over 200 double rubs satisfactory.

RESULTS AND DISCUSSION

Chemistry and Catalysts

The chemistry involved in the coating utilizes the crosslinking reaction between HMMM and the acrylic polyol. The reaction produces an etherification of the polyol hydroxy groups with the methoxymethyl groups on the melamine and liberates methanol. The schematics are illustrated in *Figure* 1. The use of a strong acid catalyst is required to produce a cure at a reasonably low temperature. Such a low baking temperature is desirable to save energy and to enable the coating of heat-sensitive substrates. Aromatic sulfonic acid cationic curing catalysts, for melamine-based coatings, have been available for some time. They include catalysts such as PTSA, DDBSA, as well as other alkylated aromatic sulfonic acids. More recently, alkane sulfonic acids have become available, which are also active cure catalysts. They also directly catalyze the etherification reaction. Latent catalysts include various amine blocked sulfonic acids. In order for the reaction to occur, the deblocking reaction generating the active acid is required to occur first. The general structures for the two types of catalysts are shown in *Figure* 2.

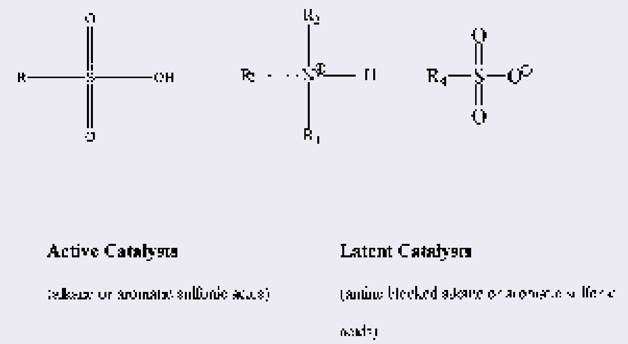

Figure 2—General structure for active and latent sulfonic acid derivatives.

Qualitative FTIR Results

The reference spectra for the two components of the coating, HMMM and the acrylic polyol are illustrated in *Figure* 3. The OH stretching vibration for the acrylic polyol is centered at 3500 cm^{-1} and is the dominant spectral feature in this spectral region. The figure also shows the aromatic C–H stretching vibrations associated with the styrene units. As noted in the Experimental Section, these vibrations are utilized to normalize the spectra and compensate for any thickness effects. HMMM also exhibits a transition in this spectral region. It is

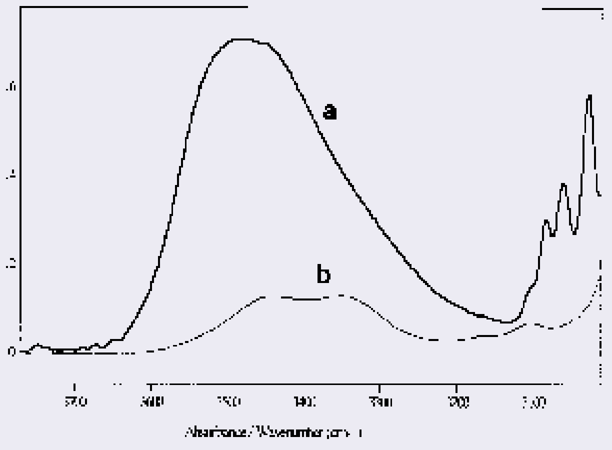

Figure 3—Reference FTIR spectra for polyol (curve a) and HMMM (curve b).

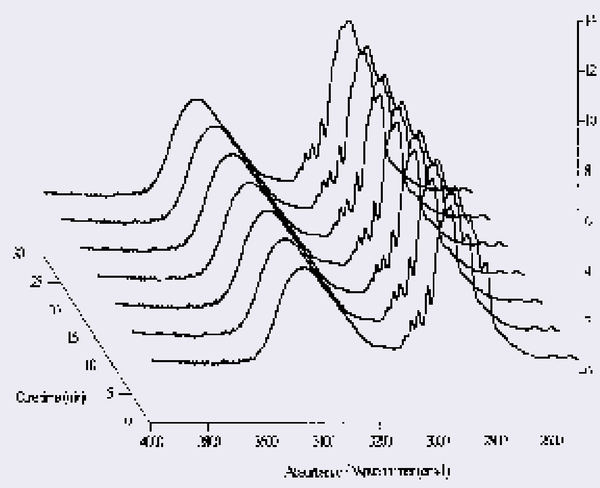

Figure 4—FTIR spectra as a function of cure time at 120°C, no catalyst.

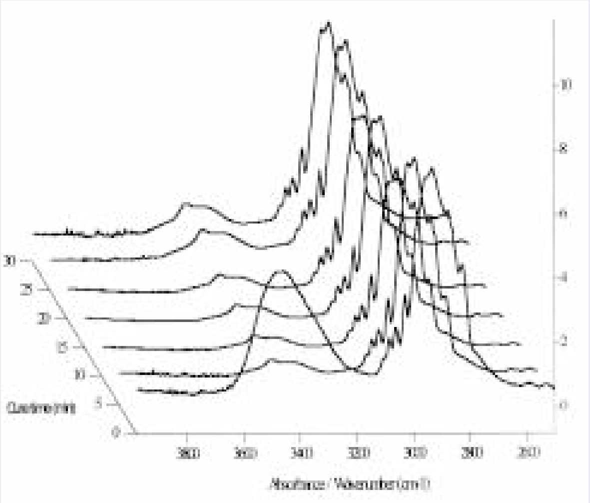

Figure 5—FTIR spectra as a function of cure time at 120°C, MSA catalyst.

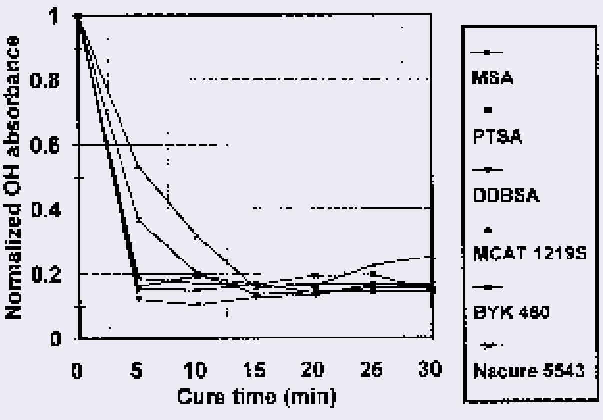

Figure 6—Efficiency of various sulfonic acid catalysts. Active catalysts: MSA, PTSA, and DDBSA; latent catalysts: MCAT 1219S, BYK 460 and Nacure 5543. Samples cured at 120°C.

significantly weaker than the OH stretching vibration, most likely an overtone, and its contribution at 3472 cm^{-1} is reflected in a residual absorbance of approximately 0.2 normalized units. Thus, its detection is not an indication of incomplete cure. Furthermore, in control experiments, it was found that its intensity is invariant with the degree of cure and thermal treatment for a constant composition.

Figures 4 and 5 illustrate composite plots of absorbance profiles as a function of cure time at 120°C in the absence of catalyst and in the presence of MSA catalyst. In the absence of a catalyst, no change in the absorbance profile for the OH stretching vibration is observed, even after 30-min cure. In contrast, when MSA is added, an immediate change is observed. *Figure* 5 also shows the high catalytic activity associated with an active catalyst such as MSA which does not require deblocking.

Quantitative FTIR Results

Figure 6 illustrates the efficiency of a number of active and latent catalysts. All alkane sulfonic acid catalysts promote fast cure. The catalytic activity of amine blocked alkane sulfonic acids depends on the kinetics and thermodynamics of the deblocking reaction. Nacure 5543 undergoes fast deblocking, under the experimental conditions, and its activity is similar to that of free alkane sulfonic acids. For blocked catalysts exhibiting slower deblocking, the catalytic rate is decreased as illustrated for BYK 460 and MCAT 1219S. In his work, Bauer[15] also noted slower rates for the amine salts for PTSA. An activity/latency diagram is shown in *Figure* 7 and schematically classifies the catalysts. Based on such a diagram, an appropriate choice of catalysts can be made to tailor a specific application.

Comparison with Physical Measurements

The major interest in the grazing angle FTIR methodology was to explore its applicability as a predicator for coating properties. *Figure* 8 illustrates a direct comparison between the IR normalized OH profile as a function of cure time and the results of the MEK double rub test. Shown in the figure, as the concentration of OH functionality in the film decreases, the number of double rubs necessary to damage the coating film on the steel panel increases. A good correlation between the two is established, especially at early cure times. At the latter stages of the reaction, IR is a less sensitive predicator. Small decreases in the concentration of OH groups may not translate into detectable changes in the intensity of the IR absorbance associated with the OH stretching vibration, but the resulting small increase in the degree of cure may affect properties in a much more dramatic fashion. This is noted in *Figure* 8 where the MEK double rub test results continue to increase for the latter stages of the reaction. The IR measurement correspondence with the physical test (MEK double rub) opens the possibility of substituting IR measurements for catalyst performance screening. The FTIR technique results in significant time reductions for coating evaluation.

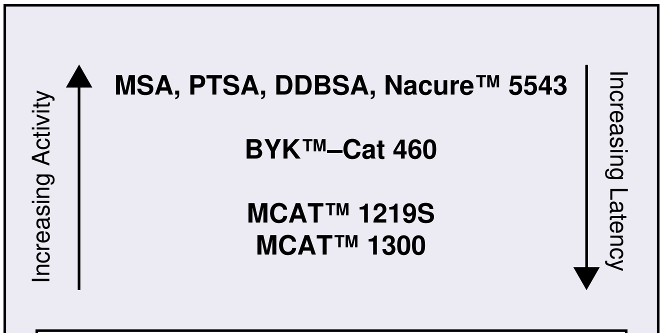

Figure 7—Activity/latency diagram.

CONCLUSION

The objective of these experiments was to study the curing chemistry of melamine resin coatings using various catalysts by means of FTIR techniques. The results illustrate the capabilities of grazing angle FTIR spectroscopy to monitor the extent of cure for the coating systems studied. The data shows a decrease of the OH stretching intensity at 3400-3500 cm^{-1}, which indicates a reaction between HMMM (melamine resin) and the acrylic polyol forming ether type linkages with methanol given off. In terms of catalytic activity, MSA, PTSA, Nacure® 5543, and DDBSA cure the fastest. BYK™ 460 and MACT™ 1219S are slower in promoting the cure, affording a larger processing window for these applications requiring flexibility. The IR measurements have shown good correspondence with physical tests (MEK double rub), opening the possibility of substituting IR measurements for screening performance. The FTIR techniques result in a significant time reduction for evaluation and provide opportunities for classification of the chemistry involved in the curing.

References

(1) Putzig, C.L., Leugers, M.A., McKelvy, M.L., Mitchell, G.E., Nyquist, R.A., Papenfuss, R.R., and Yurga, L., *Anal. Chem.*, 64, 270 (1992).
(2) Putzig, C.L., Leugers, M.A., McKelvy, M.L., Mitchell, G.E., Nyquist, R.A., Papenfuss, R.R., and Yurga, L., *Anal. Chem.*, 66, 26 (1994).
(3) Claybourn, M. and Turner, P., "Structure Property Relations in Polymers," *Advances in Chemistry Series 236*, p. 408, American Chemical Society, 1993.
(4) Carlson, G.M., Neag, C.M., Kuo, C., and Provder, T., *Fourier Transform Infrared Spectroscopy Characterization of Polymers*, p. 197, Plenum Press, New York, 1987.
(5) Yang, C.-P. and Lee L.-T., *J. Appl. Polym. Sci.*, 35, 449 (1988).
(6) Yang, Y.S. and Lee, L.J., *J. Appl. Polym. Sci.*, 37, 2313 (1989).
(7) Pryde, C.A., *J. Polym. Sci., Part A: Polym. Chem.*, 27, 711 (1989).
(8) Louden, D., *J. Appl. Polym. Sci.*, 57, 1575 (1985).
(9) Lazzara, M.G., "Techniques to Measure Melamine/Polyol Reactions in a Film," JOURNAL OF COATINGS TECHNOLOGY, *56*, No. 710, 19 (1984).
(10) Yamamoto, T., Nakamichi, T., and Ohe, O., "Kinetics of Carboxylic Acid Catalyzed Melamine/Polyol Reaction in a Film," JOURNAL OF COATINGS TECHNOLOGY, *60*, No. 762 (1988).
(11) Blank, W.J., "Polyurethane Oligomers for Waterborne and High-Solids Coatings," JOURNAL OF COATINGS TECHNOLOGY, *60*, No. 764, 43 (1988).
(12) Hill, L.W. and Lee, S.-B., "Effect of Melamine-Formaldehyde Structure on Cure Response of Thermoset Coatings," JOURNAL OF COATINGS TECHNOLOGY, *71*, No. 897, 127 (1999).
(13) Haseebuddin, S., Raju, K.V.S.N., and Yaseen, M., "Crosslink Density and Cure Window of Oligourethane Diol/Melamine High-Solids Coatings," JOURNAL OF COATINGS TECHNOLOGY, *70*, No. 879, 35 (1998).
(14) Collette, J.W., Corcoran, P., Tannenbaum, H.P., and Zimmt, W.S., *J. Appl. Polym. Sci.*, 32, 4209 (1986).
(15) Bauer, D.R. and Budde, G.F., *J. Appl. Polym. Sci.*, 28, 253 (1983).
(16) Song, Y.P., Petty, M.C., and Yarwood, J., *Vibrational Spectroscopy*, 1, 305 (1991).
(17) Rabolt, J.F., Jurich, M., and Swalen, J.D., *Appl. Spectrosc.*, 39, 269 (1985).
(18) Schlotter, N.E. and Rabolt, J.F., *Appl. Spectrosc.*, 39, 994 (1985).

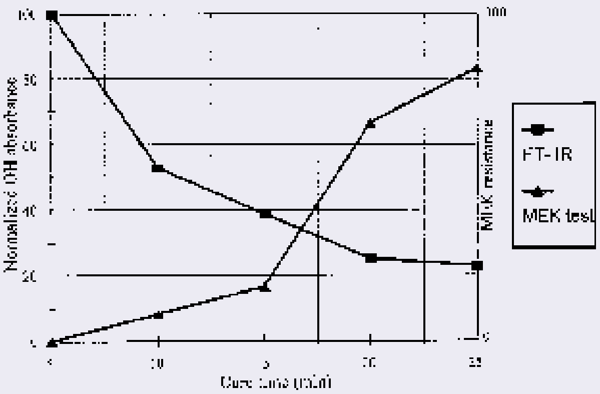

Figure 8—Comparison of IR and MEK double rub test performance for MCAT 1219S as a function of cure time at 120°C.