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COBALT ION-CONTAINING EPOXIES

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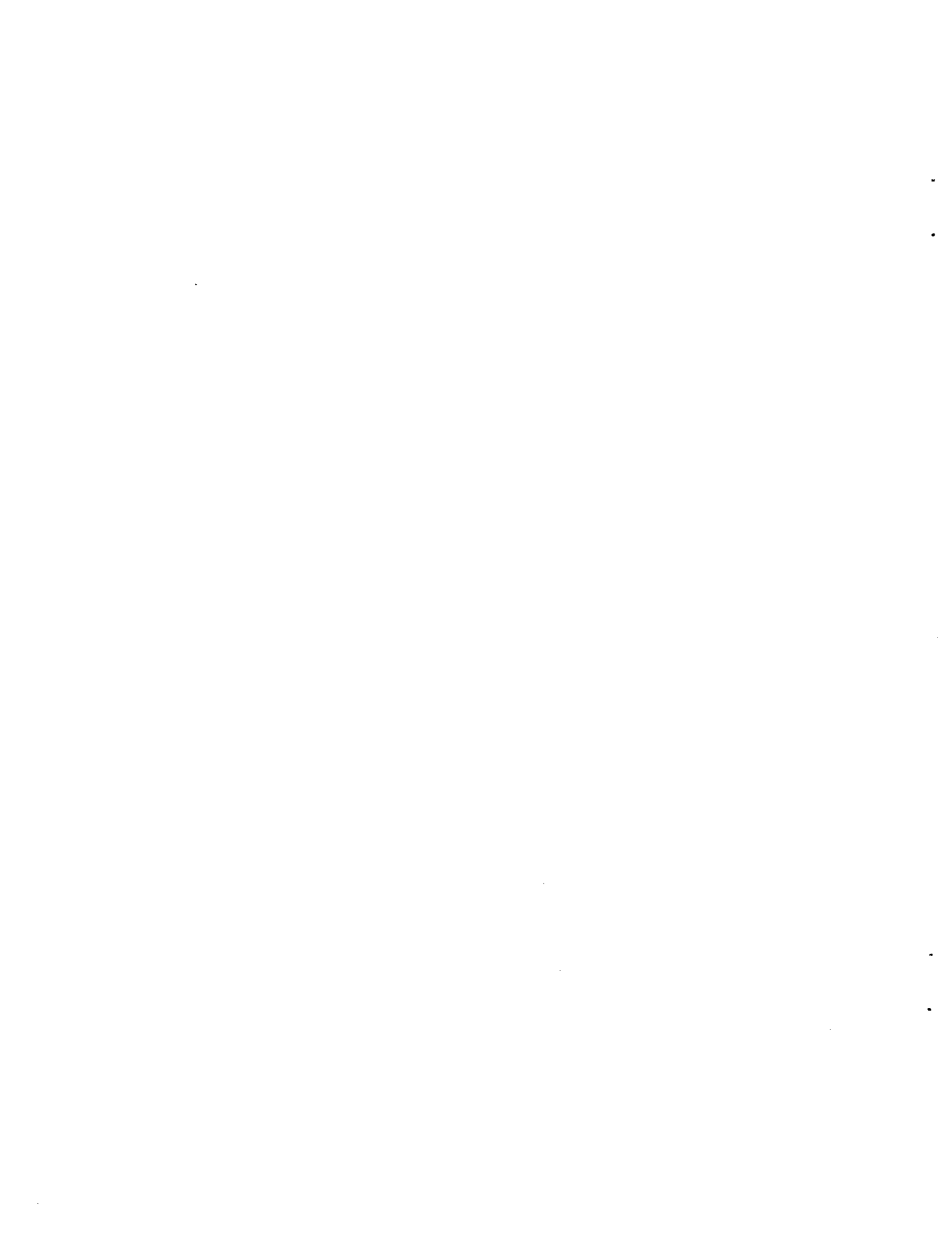
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INTRODUCTION

Because of their excellent processability, chemical resistance, low density and low cost, epoxy resins have been widely used by the aerospace industry as composite matrix resins. However, these highly crosslinked polymers tend to be brittle, possessing low mechanical strengths. A preliminary study at NASA-Langley showed that the incorporation of approximately one percent cobalt ions into a commercial epoxy matrix resin substantially increased the mechanical strength of that resin (1). This increase was achieved with only a slight sacrifice in thermal stability and with no increase in the polymer density.

Because of these initially promising results, further research has been conducted to determine the effect of varying the concentration of cobalt ions in an aerospace composite matrix resin. The approach taken was to formulate and characterize cobalt ion-containing epoxies prepared by adding cobalt (III) acetylacetonate ($\text{Co}(\text{acac})_3$) to an MY-720* based resin system.

COBALT ION-CONTAINING EPOXIES

OBJECTIVE: DETERMINE THE EFFECT OF INCORPORATING COBALT IONS INTO AN AEROSPACE EPOXY RESIN

APPROACH: PREPARATION AND CHARACTERIZATION OF MY-720 BASED EPOXIES CONTAINING VARYING CONCENTRATIONS OF COBALT (III) ACETYLACETONATE

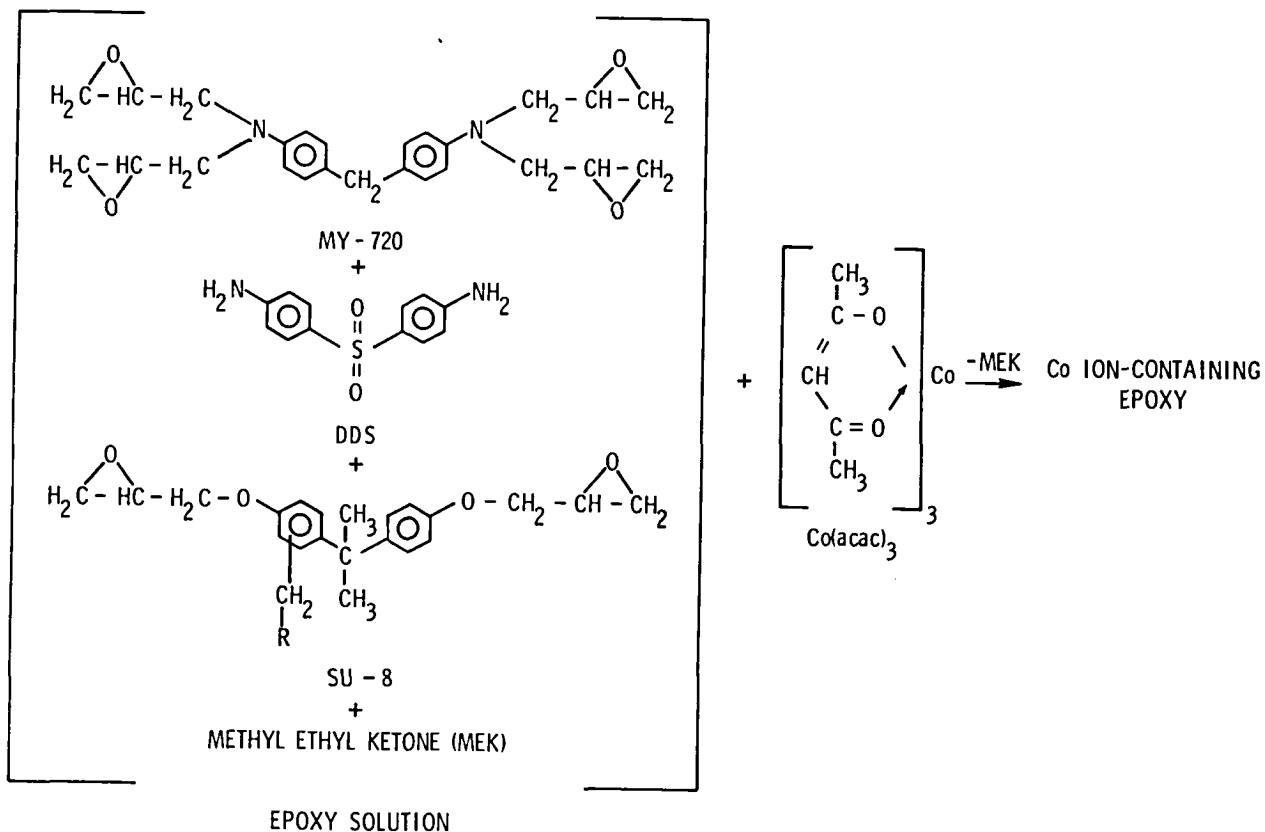
*MY-720 is a product of Ciba-Geigy Corporation. Use of trade names or names of manufacturers in this report does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

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STANDARD METHOD OF Co/EPOXY PREPARATION

The epoxy resin that served as the control in this study consisted of 73.4% tetraglycidyl methylene dianiline (MY-720) with 20.6% 4,4'-diaminodiphenylsulfone (DDS) curing agent and 6.0% of an epoxidized phenolic novalac (SU-8)*. This thermosetting formulation is similar to several important commercial resins, including Narmco 5208.** In this study, the standard method of epoxy preparation involved dissolving 62.5% MY-720/DDS/SU-8 in methyl ethyl ketone (MEK). This dilution facilitated the addition of $\text{Co}(\text{acac})_3$, added to the epoxy solution at several concentrations based on the molar ratio of metal complex to MY-720 polymer repeat units. The Co/epoxy mixtures were stirred at room temperature until their appearance changed from grainy, dark green to an opalescent green. These solutions were poured into aluminum pans, degassed at 120°C under vacuum for 45-50 minutes, then cured by gradually increasing the oven temperature to 150°C over a 3-3 1/2 hour period, with a 1 hour hold at 150°C and a 2 hour postcure at 177°C.

STANDARD METHOD OF Co/EPOXY PREPARATION

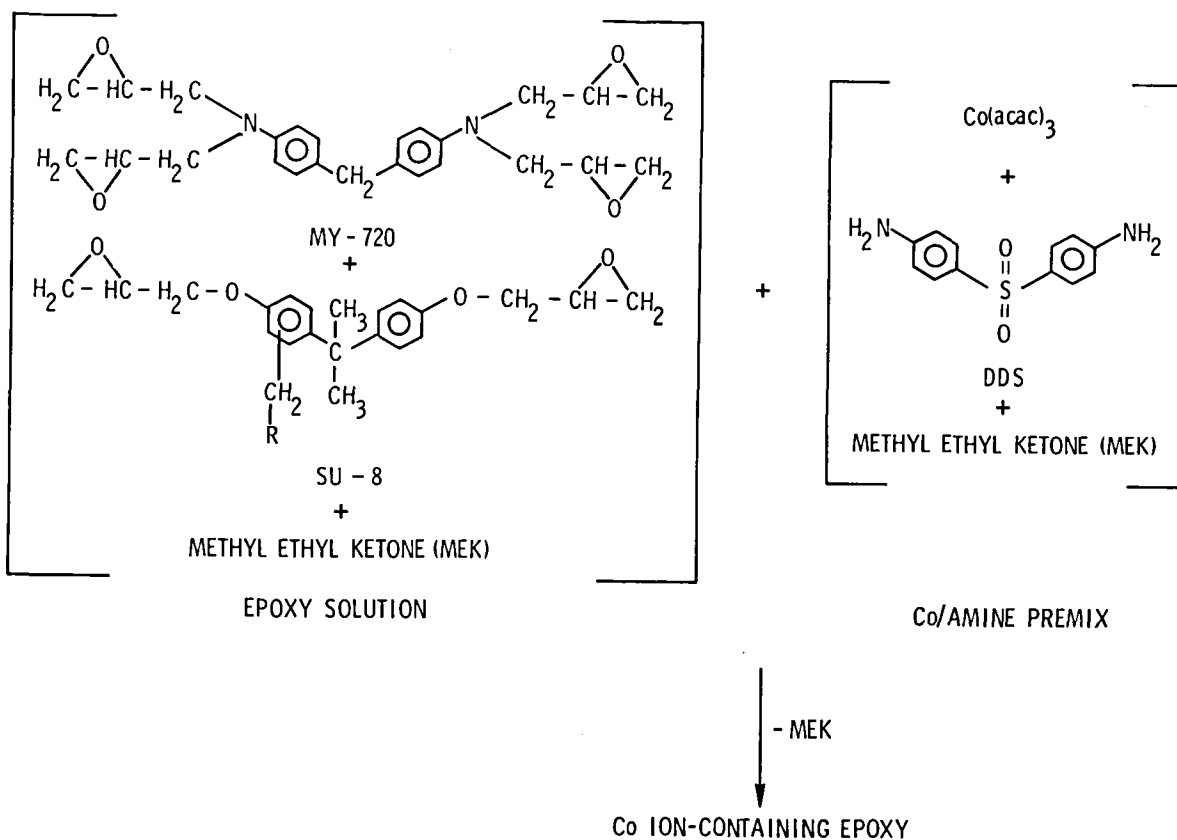


*SU-8 is a product of Celanese Chemical Co., Inc.
 **5208 epoxy resin is a product of Narmco Materials, Inc.

PREMIX METHOD OF Co/EPOXY PREPARATION

An alternate method of preparing cobalt ion-containing epoxies was also used. In this method varying concentrations of $\text{Co}(\text{acac})_3$ were premixed with DDS dissolved in MEK. It was felt that the opalescence noted in the standard method preparation was the result of a reaction occurring between cobalt and the diamine curing agent during the room temperature stirring. Any such reaction (for example, formation of a cobalt/amine complex) could be facilitated by premixing these components before addition with the epoxides. The epoxy solution prepared for addition with the premixes contained 61.5% MY-720, 5.0% SU-8 and 33.5% MEK. After adding the Co/amine premixes to the epoxy solution, the procedures used for degassing and curing the standard method Co/epoxies were followed. The ratio of cobalt ions to MY-720 polymer repeat units in the cured resins varied from 1:50 to 1:5 using either method of Co/epoxy preparation.

PREMIX METHOD OF Co/EPOXY PREPARATION



CURE PROPERTIES

Gel times were determined at 135°C on a Gel Timer Hot Pot manufactured by Shyodu Precision Instrument Co., using 35g of degassed epoxy resin prepared according to the premix method. All resins were degassed under vacuum at 100°C for 30 minutes just prior to gel time determinations. The MY-720/DDS/SU-8 control gelled in 190 minutes at 135°C. The addition of varying amounts of cobalt ions accelerated the epoxy cure. This acceleration increased with increasing cobalt ion concentration to a gel time of only eight minutes for the 1/5 Co/epoxy resin.

Co/epoxies prepared by the standard method showed this accelerated cure, but to a lesser extent than for the premix systems at a given cobalt ion concentration. For example, the 1/10 Co/epoxy gelled in 26 minutes when prepared by the premix method, but took 45 minutes to gel when the standard method of preparation was used. This was an indication that premixing the cobalt acetylacetonate and the diamine curing agent allowed the interaction between these two components to occur more efficiently or to a greater extent than when using the standard method of preparation.

Heats of reaction (ΔH 's) were determined on a DuPont 990 Thermal Analyzer/Differential Scanning Calorimeter (DSC) using a programmed heating rate of 10°C/min. The DSC cell calibration constant was determined using a tin standard. Prior to the time base DSC runs, the epoxy solutions were degassed under vacuum for 30 minutes at 100°C to remove the methyl ethyl ketone solvent. In addition to the epoxy/amine cure exotherm that is standard for the MY-720/DDS/SU-8 control, the cobalt ion-containing systems exhibited a second exotherm occurring between 120-180°C that was attributed to the presence of cobalt ions. Typical DSC scans are shown and further discussed on page 6.

CURE PROPERTIES (CONTINUED)

All peak areas were determined using a planimeter and for the Co/epoxies were calculated as the total area under both cure exotherm peaks. The heats of reaction were found to decrease with increasing cobalt ion concentration. The ΔH for the 1/5 Co/epoxy was 20% lower than for the control, although the 1/5 system was found to be the "hottest" system by gel time determinations. It is felt that this apparent decrease in ΔH may be at least partially the result of some initial reaction occurring in the cobalt catalyzed epoxies during the degassing of the MEK solvent before the DSC scans were run. The degassing for the ΔH determinations was conducted at a lower temperature and for a shorter period of time than during the actual epoxy cures in an attempt to minimize this problem. Any reaction that did occur during degassing, however, would be expected to occur to a greater extent as the cobalt ion concentration was increased, resulting in the loss of increasingly larger portions of the total heat of reaction that were detected by the subsequent DSC scan.

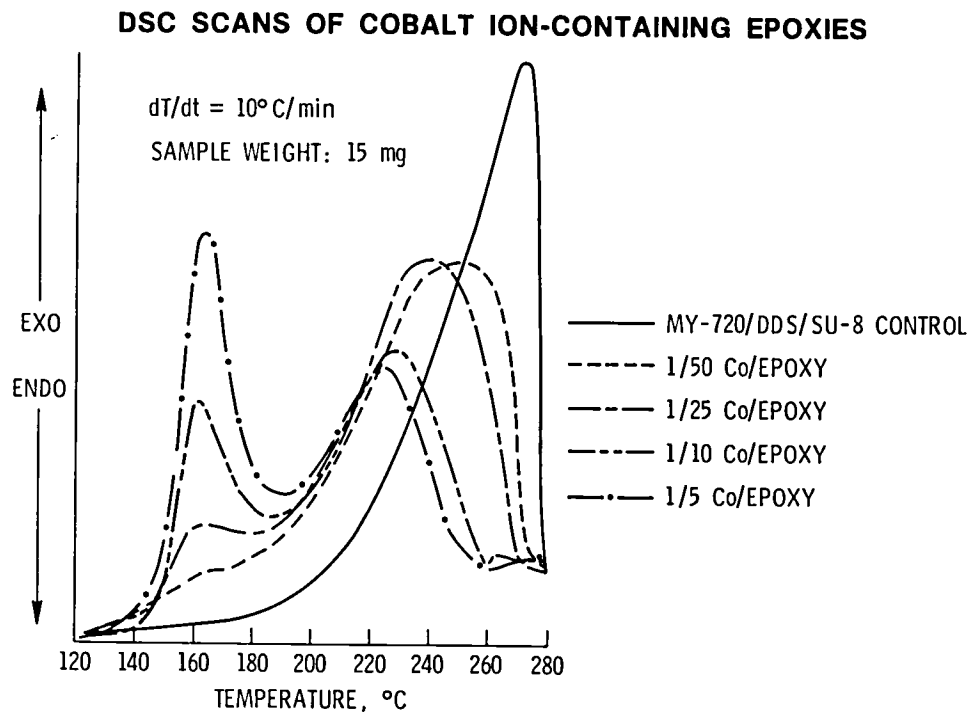
CURE CHARACTERISTICS OF COBALT ION-CONTAINING EPOXIES

MOLE RATIO, Co/EPOXY	GEL TIME AT 135°C, minutes	HEATS OF REACTION, J/g
0	190	496
1/50	127	483
1/25	102	471
1/10	26	440
1/5	8	395

CURE EXOTHERMS

DSC curves of the cobalt ion-containing epoxies were obtained on a DuPont 990 Thermal Analyzer/Differential Scanning Calorimeter using a programmed heating rate of 10°C/min. Prior to the DSC runs, each epoxy solution was degassed under vacuum for 30 minutes at 100°C to remove the MEK solvent. As shown below, the MY-720/DDS/SU-8 control had a single exotherm at 273°C. However, a second and lower temperature exotherm was observed for the cobalt ion-containing epoxies. This additional exotherm peaked in the temperature range of 160-165°C which is within the curing temperature range of this epoxy resin. As is evident from the scans, the intensity of this early exotherm increased dramatically with increasing cobalt ion concentration.

The higher temperature cure exotherm was found to occur at increasingly lower temperatures with increasing cobalt ion concentration, at 260°C for the 1/50 Co/epoxy, for example, and at 226°C for the 1/5 Co/epoxy. This effect, combined with the appearance of the additional exotherm in the Co/epoxies, resulted in the acceleration of the epoxy cure that was demonstrated by the gel time measurements discussed previously.



COBALT ION-CONTAINING EPOXIES

Discs of the cobalt ion-containing epoxies were prepared according to the standard and premix methods. Densities were determined on samples of the cured polymer in a density gradient tube according to ASTM D1505-60T. The densities were essentially unchanged by the addition of the cobalt complex. Densities of Co/epoxies prepared by the premix method are listed in the table below. No differences in density were noted between these samples and those prepared by the standard method.

Elemental analysis indicated that the percent cobalt in the epoxies ranged from 0.18 to 1.69 as the $\text{Co}(\text{acac})_3/\text{MY-720}$ mole ratio was increased from 1/50 to 1/5. These values were independent of the method of sample preparation.

The appearance of the cured epoxy specimens changed from a transparent amber control to increasingly darker and less transparent discs with increasing $\text{Co}(\text{acac})_3$ concentration.

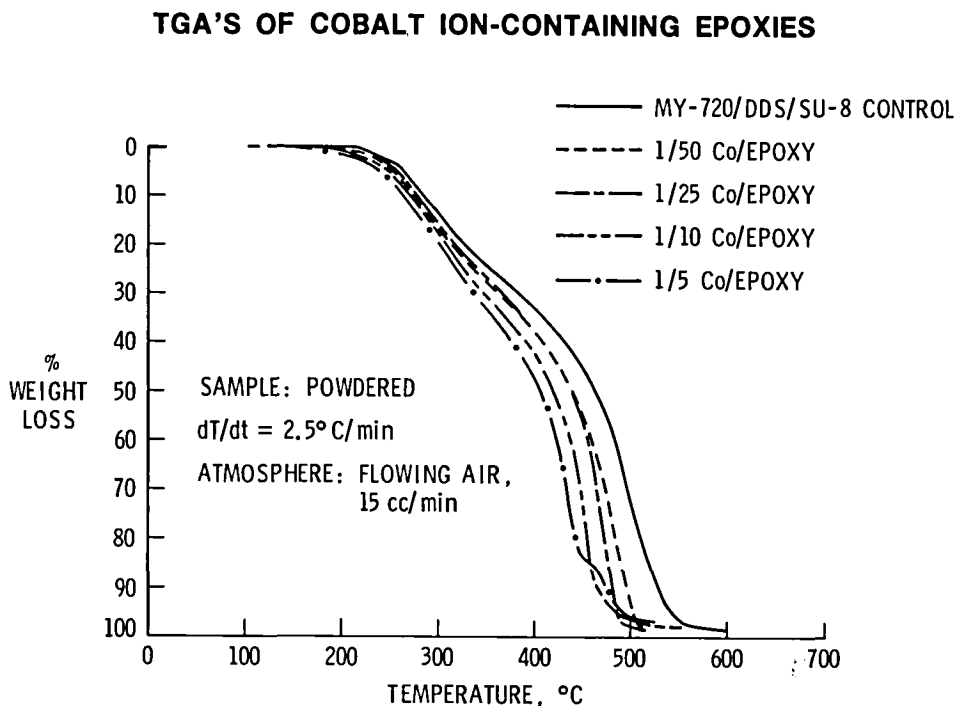
COBALT ION-CONTAINING EPOXIES

MOLE RATIO Co/EPOXY	DENSITY, g/cc	PERCENT COBALT	APPEARANCE OF CURED DISCS
0	1.271	0	TRANSPARENT AMBER
1/50	1.271	0.183	TRANSPARENT TOPAZ
1/25	1.266	0.378	TRANSPARENT TOPAZ
1/10	1.266	0.912	TRANSPARENT BROWN
1/5	1.266	1.690	OPAQUE DK. BROWN

THERMOGRAVIMETRIC ANALYSIS (TGA)

The thermooxidative stability of powdered epoxy samples was measured in flowing air (15 cc/min.) on a Perkin Elmer Model TGS-2 Thermogravimetric System using an AR-2 Autobalance and a UU-1 Temperature Program Control at a heating rate of 2.5°C/min after an initial 30 min hold at 100°C. The curves below show the percent weight loss of powdered samples of Co/epoxies prepared by the premix method. Curves for epoxies prepared by the standard method were essentially identical.

A slight loss of thermal stability was noted for the cobalt ion-containing epoxies, a trend that increased with increasing cobalt ion concentration and resulted in a difference of approximately 50°C between the temperature at 50% weight loss for the control and the 1/5 Co/epoxy.



GLASS TRANSITION TEMPERATURES

Apparent glass transition temperatures (T_g's) of the cured epoxies were determined on a DuPont Model 943 Thermomechanical Analyzer (TMA) at a heating rate of 10°C/min using a penetration probe. Regardless of the method used for preparing the Co/epoxies, the addition of cobalt (III) acetylacetonate to the MY-720-based epoxy consistently lowered the T_g. This decrease in glass transition temperature became increasingly pronounced as the cobalt ion concentration or acceleration of cure increased. Differences between the methods of sample preparation also became apparent in these T_g measurements. At any given concentration of cobalt ions, the glass transition temperature was lower for the samples prepared using the more highly accelerated premix method. When a sample of the 1/10 Co/epoxy was postcured an additional 2 hours at 177°C, the glass transition temperature was increased by 15°C.

GLASS TRANSITION TEMPERATURES OF Co/EPOXIES

MOLE RATIO Co/EPOXY	T _g BY TMA, °C	
	STANDARD PREP	PREMIX METHOD
0	206	—
1/50	198	193
1/25	185	180
1/10	186	167
1/5	158	131

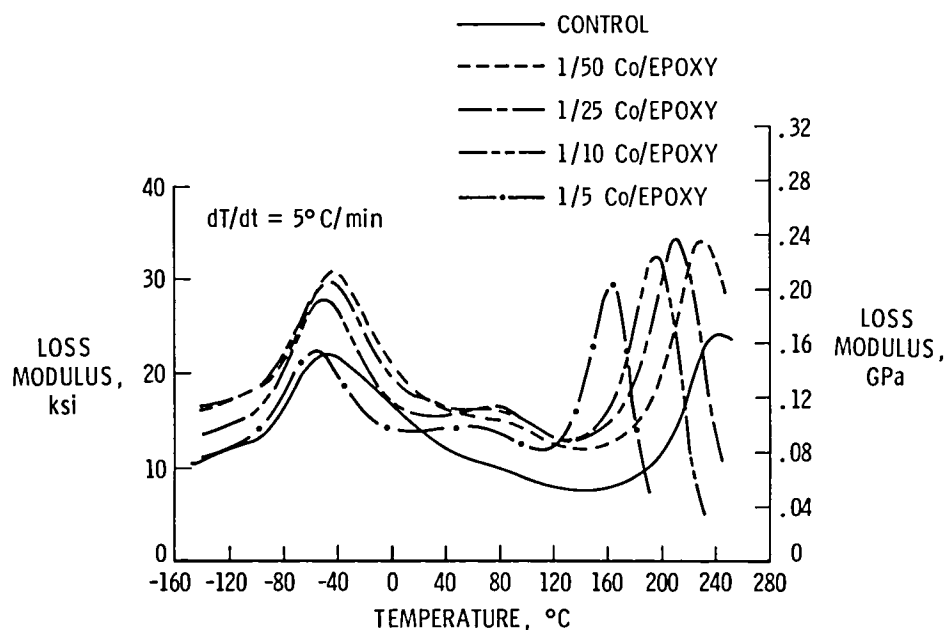
DYNAMIC MECHANICAL ANALYSIS SPECTRA

Dynamic Mechanical Analysis (DMA) curves of the cobalt ion-containing epoxies are compared with that of the control in the figure below. The loss modulus curves were obtained on a DuPont 1090 Thermal Analyzer with a 981 Dynamic Mechanical Analyzer at a programmed heating rate of 5°C/min.

All materials showed a low temperature β -transition occurring between -45 to -58°C. The magnitude of this β -transition peak increased dramatically with the first Co addition (1/50). Although the magnitude of this β -transition decreased with increasing cobalt ion concentration, it was still greater for the 1/25 and 1/10 Co/epoxies than for the control. Only when the cobalt ion concentration was increased to the 1/5 level did the β -transition return to the level of the control. An MY-720/DDS/SU-8 system catalyzed by boron trifluoride monoethylamine has been reported to show a similar increase in the magnitude of the β -transition (2). This increase was attributed by Munns and Seferis to additional amine-epoxy reaction resulting from heat supplied by the exothermic nature of the BF_3 catalyzed reaction.

The α -transitions of the Co/epoxies supported the trend shown by TMA of decreasing glass transition temperature with increasing cobalt ion concentration. Additional postcure of the Co/epoxies was found to shift the α -transition to higher temperatures.

DMA'S OF COBALT ION-CONTAINING EPOXIES



MECHANICAL STRENGTH AND STIFFNESS

Flexural properties were determined at room temperature on neat resin castings of the cobalt ion-containing epoxies. Tests were run using an Instron Testing Machine Model TT-C in a three point bending mode on specimens whose dimensions averaged 6.23 mm x 1.27 mm x 49.23 mm. An average span to thickness of 16/1 was used, as specified by ASTM Standard D790-71. The data points listed in the table below represent the average of six specimens with an average deviation from the mean of $\pm 7\%$ for the flexural strength and $\pm 5\%$ for the flexural modulus. Increases of up to 33% in flexural strength were achieved with the cobalt-containing epoxies prepared by the premix method. As the modulus values indicate, there is a trend toward decreasing stiffness with increasing cobalt ion concentration.

This pronounced improvement in mechanical strength of the cobalt ion-containing epoxies may be attributed to their mechanism of cure and resulting network structure. It has been shown that slow curing rates in epoxies result in networks having larger microgels, higher Tg's and higher internal stresses (3). Furthermore, the coherence of the polymer network and the resulting mechanical behavior have been found to be dependent on the strength of the connections between the secondary microgels (4). It is possible that this cobalt accelerated cure, which does result in lower Tg's, also results in the formation of a stronger, more continuous secondary microgel network.

FLEXURAL PROPERTIES OF COBALT ION-CONTAINING EPOXIES

MOLE RATIO Co/EPOXY	FLEX. STR., ksi	FLEX. MOD., ksi
0	18.9	692
1/50	25.1	679
1/25	21.9	613
1/10	19.2	593
1/5	24.3	539

CONCLUSIONS

Cobalt ion-containing epoxies were prepared by incorporating different concentrations of $\text{Co}(\text{acac})_3$ in an MY-720 based epoxy resin. The addition of cobalt ions accelerated the epoxy cure as indicated by gel time determinations and by the occurrence of an early cure exotherm evident on DSC scans. Cured castings of the Co/epoxies had lower glass transition temperatures than the control as measured by both thermomechanical analysis and dynamic mechanical analysis. Mechanical properties, determined at room temperature on neat resin specimens, showed increases in flexural strength of up to 33% with the cobalt ion-containing epoxies. This improvement in strength was obtained with no increase in density and only a slight sacrifice in thermal stability.

These high strength cobalt ion-containing epoxies will be scaled-up and further evaluated for their performance as a composite matrix resin.

EPOXIES CONTAINING COBALT IONS



- VARYING CONCENTRATIONS OF COBALT IONS HAVE BEEN INCORPORATED INTO A HIGHLY CROSSLINKED AIRCRAFT EPOXY
- THE ADDITION OF $\text{Co}(\text{III})$ IONS ACCELERATES THE EPOXY CURE AND ALTERS THE RESULTING NETWORK STRUCTURE
- COBALT IONS IMPROVE MECHANICAL STRENGTH WITHOUT INCREASING DENSITY

POTENTIAL APPLICATIONS

MATRIX RESINS FOR ADVANCED AIRCRAFT AND SPACECRAFT

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16. Abstract Varying concentrations of an organometallic cobalt complex have been added to an epoxy system currently used by the aerospace industry as a composite matrix resin. Methods for combining cobalt (III) acetylacetonate with a tetraglycidyl 4,4'-diaminodiphenylmethane-based epoxy have been investigated. The effects of increasing cobalt ion concentration on the epoxy cure have been demonstrated by epoxy gel times and differential scanning calorimetry cure exotherms. Analysis on cured cobalt-containing epoxy castings included determination of glass transition temperatures by thermomechanical analysis, thermooxidative stabilities by thermogravimetric analysis, and densities in a density gradient column. Flexural strength and stiffness were also measured on the neat resin castings.					
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