NASA
Techr
Paper
2639

December 1986

Investigation of the Effects of Cobalt Ions on Epoxy Properties

Jag J. Singh and
Diane M. Stoakley

NASA

Investigation of the Effects of Cobalt Ions on Epoxy Properties

Jag J. Singh and
Diane M. Stoakley

Langley Research Center
Hampton, Virginia

Summary

The effects of Co(acac)$_x$ complexes on MY-720 epoxy properties have been investigated. It appears that Co^{2+} ions form antibonding or nonbonding orbitals which increase the free volume and also reduce the cohesiveness of the host epoxy. The effects of Co^{3+} ions, on the other hand, seem to result in increased cohesiveness of the epoxy. The experimental values of magnetic moments of both types of ions in MY-720 suggest that the orbital momentum contributions of the (3d) electrons are partially conserved, though the effect is more pronounced for Co^{2+} ions. The coordination environment of the cobalt ions in the host epoxy does not appear to be uniquely defined. These results indicate that the effects of metal ions on resin properties cannot be easily predicted on the basis of Ligand field theory arguments alone. Complex interactions between metal ions and host epoxy molecular structure suggest the desirability of parallel experimental investigations of electronic, magnetic, and mechanical properties of metal ion-containing epoxy samples for comparison with theory.

Introduction

It has been reported (ref. 1) that the presence of cobalt ions in Narmco 5208 epoxy resin results in a significant improvement in its mechanical properties, presumably because of the formation of a stronger, more continuous, secondary microgel network. The authors claim that the addition of 1:10 mole ratio of cobalt(III) acetylacetonate, Co(acac)$_3$, to tetraglycidyl methylene dianiline (MY-720) epoxy resulted in an impressive 95-percent increase in flexural strength, a 35-percent increase in modulus, and a 41-percent decrease in tensile elongation. In a later study (ref. 2), they compared the effects of Co(acac)$_3$ compound with those produced by other cobalt compounds and concluded that Co(acac)$_3$ is unique in improving flexural strength and fracture toughness of the epoxy. In an effort to better understand the mechanisms by which cobalt ions effect improvements in mechanical strength and stiffness of the host epoxies, we have investigated the effects of cobalt(II) acetylacetonate, Co(acac)$_2$, and Co(acac)$_3$ metal complexes in MY-720—a major component of the Narmco 5208 epoxy resin. Metal complexes were added at the molar ratios of 1 metal complex for every 10 to 50 MY-720 repeat units, and the resulting specimens were investigated for their free volume, free electron density, and magnetic properties. The results are summarized in the sections which follow.

Symbols

FWHM	full width at half maximum height
g	acceleration due to gravity
H	magnetic field strength
$\frac{\partial H}{\partial \ell}$	magnetic field gradient at sample location
I_2	intensity of long-life component
k	Boltzmann constant
k_1	displaced medium susceptibility per unit volume
M	mass of sample out of field
m	net change in sample mass in field
Ps	positronium
T	absolute temperature
V	volume of displaced medium (sample volume)
β	magnetic balance calibration constant
$\bar{\mu}_{\text{eff}}$	effective magnetic moment of metal ion
μ_0	Bohr magneton
τ_1	lifetime of short-life component
τ_2	lifetime of long-life component
χ_g	gram susceptibility
χ_m	molar susceptibility

Sample Preparation

MY-720/DDS epoxy samples containing either Co^{3+} or Co^{2+} ions were prepared as described in the sections below.

Preparation of Co(acac)$_3$-Epoxy Solution

In an effort to maximize the interaction between Co(acac)$_3$ and the diamine curing agent in the epoxy system, a premix method of preparing the solution was used. (See ref. 2.) In this method, preweighed quantities of Co(acac)$_3$ complex were first added to the solution of 1.98 grams of 4,4' diaminodiphenylsulfone (DDS) dissolved in 6.00 grams of methyl ethyl ketone (MEK) and stirred for several hours at room temperature. This solution was then added to a solution of 7.00 grams of MY-720 dissolved in 3.00 grams of MEK. Thus, the final MY-720/DDS/MEK solution composition was 7.00 grams/1.98 grams/9.00 grams with variable

amounts of the Co(acac)$_3$ complex. Figure 1 shows the premix method of preparing the Co(acac)$_3$-epoxy solution.

Preparation of Co(acac)$_2$-Epoxy Solutions

These solutions were prepared by the standard method, because no differences in final properties were detected between the solutions prepared by the premix method and those prepared by the standard method. Following the standard method, a solution containing 7.00 grams of MY-720 and 1.98 grams of DDS dissolved in 5.38 grams of MEK was first prepared. Next, variable amounts of the Co(acac)$_2$ complex were added to this solution and were stirred for several hours at room temperature. Figure 2 shows the standard method of preparing the Co(acac)$_2$-epoxy solution.

Preparation of Test Samples

To prepare the samples in the form of 2.54-cm diameter by 0.32-cm thick discs, the epoxy solutions containing cobalt ions were poured into aluminum pans, degassed at 120°C under vacuum for 45 to 50 minutes, and cured by gradually increasing the temperature to 150°C over a 3-hour period, with a 1-hour hold at 150°C and a final cure at 177°C. The compositions of the various samples thus produced are summarized in table I.

Experimental Results

Saturation Moisture Content

It is anticipated that the epoxy thermomechanical properties are intimately related to the volume occupied by microvoids in them. This volume is frequently referred to as the free volume of the material. To infer the free volume in the various test samples, it was decided to measure their saturation moisture contents. It is expected that the saturation moisture content is directly related to the free volume accessible to it. The procedure for measuring saturation moisture contents of the epoxy specimens has been described in references 3 and 4. Essentially, the samples were kept immersed in hot distilled water at 90°C until their weights stabilized. The saturation moisture contents of the samples containing cobalt ions are summarized in table II. Even though the Co^{2+} complex makes MY-720 epoxy slightly more hygroscopic than the Co^{3+} complex, both complexes have generally increased the chemical sites where water molecules may attach to the epoxy chain.

Magnetic Measurements

Metal ions in the host epoxy are expected to impart a characteristic degree of magnetism to it, de-

pending on their final electron configurations and coordination symmetries. Thus, a measurement of the effective magnetic moment $\bar{\mu}_{\mathrm{eff}}$ of the metal ions in the epoxy should shed light on their unpaired spin electron density and on the consequent effects on the physical properties of the host epoxy. The magnetic susceptibilities of the various Co(acac)$_x$ epoxy specimens were measured by the Faraday method (refs. 5 and 6) at four magnetic field strengths ranging from 4 to 10 kilogauss. The force exerted on the sample when it was placed in the magnetic field was measured with a sensitive magnetic balance (10^{-7} gram). The electromagnet provided a vertical zone of constant $\left(H \frac{\partial H}{\partial \ell} \right)$ of about 1 cm in height. The magnetic susceptibility per gram (χ_g) is given by the following expression:

$$\chi_g = \frac{1}{M} \left(k_1 V + \frac{gm}{H \frac{\partial H}{\partial \ell}} \right) \qquad (1)$$

where

M	mass of sample out of field
k_1	susceptibility of displaced medium per milliliter (0.029×10^{-6} in cgs units for air at room temperature)
V	volume of medium displaced by sample
g	acceleration due to gravity
m	net change in sample mass in field H
H	magnetic field strength
$\frac{\partial H}{\partial \ell}$	magnetic field gradient at sample location

Since $k_1 V$ is an extremely small quantity, typically of the order of 3.5×10^{-10} in cgs units for air, equation (1) can be modified as follows:

$$\chi_g = \left(\frac{g}{H \frac{\partial H}{\partial \ell}} \right) \frac{m}{M} = \beta \frac{m}{M} \qquad (2)$$

where β is a calibration constant for the balance.

The β values for two standard samples used to calibrate the magnetic balance are summarized in table III. The effective magnetic moment of the metal ion $\bar{\mu}_{\mathrm{eff}}$ in the epoxy can be calculated as follows:

$$\bar{\mu}_{\mathrm{eff}} = (3kT\chi)^{1/2}$$
$$= \left(3kT \frac{\chi_m}{N\mu_0^2} \right)^{1/2} \qquad (3)$$

where

χ_m	molar susceptibility ($\chi_g \times$ molecular weight of compound)
μ_0	Bohr magneton (0.9273×10^{-20} erg/gauss)
k	Boltzmann constant
T	temperature in absolute scale
N	Avogadro number

The test samples were prepared in the form of 2 mm by 2 mm by 3 mm slices from each test epoxy specimen and were introduced into the active region of the magnetic balance. The measurements were made at four values of the magnetic field for each sample in order to get a more reliable measure of their magnetic susceptibilities. The magnetic susceptibility values used to calculate the effective magnetic moment were corrected for matrix diamagnetism. The values of the effective magnetic moments $\bar{\mu}_{eff}$ of the cobalt ions in these samples are summarized in table IV. The experimental values of $\bar{\mu}_{eff}$ represent the average values of all possible valence states coexisting in the polymer. All measurements were made at room temperature.

It is apparent from the data summarized in table IV that the magnetic moment values for the metal ions of the two complexes in MY-720 epoxy are comparable. To determine the source of magnetism in MY-720 epoxy specimens containing $Co(acac)_x$, we also directly measured the ionic magnetic moments in $Co(acac)_x$ compounds. These results are also shown in table IV and are as follows:

$$\bar{\mu}_{eff}\,[Co(acac)_2] = (4.76 \pm 0.01)\mu_0$$
$$\bar{\mu}_{eff}\,[Co(acac)_3] = (0.31 \pm 0.02)\mu_0$$

It is clear that the Co^{2+} and Co^{3+} compounds do not behave the same way in their respective molecular environments. Furthermore, the magnetic moment of Co^{2+} ions in the $Co(acac)_2$ complex is only slightly higher than its value when $Co(acac)_2$ is incorporated in the MY-720 matrix. However, the presence of the host matrix affects the Co^{3+} ions strongly and increases their magnetic moments to values even higher than those of Co^{2+} ions. From these different behaviors of Co^{2+} and Co^{3+} ions in MY-720 epoxy, it is expected that these two metal ions will affect the epoxy properties differently, with Co^{3+} exhibiting a more intense interactive effect. These expectations have been generally confirmed by the data reported in reference 2.

Positron Lifetime Measurements

Positron annihilation in organic materials provides a sensitive technique for inferring free electron density in the test samples. Thermalized positrons at the end of their range, surrounded by free electrons, will either annihilate with one of the free electrons, with a lifetime typically in the range of 100-400 picoseconds, or form positronium (Ps) atoms with one of the free electrons. These Ps atoms have two ways of decaying, depending on whether they are in parapositronium state (antiparallel spins) or orthopositronium state (parallel spins). It is the decay of the orthostate positronium which is sensitively dependent on the free electron density at the Ps site. Thus, a positron annihilation spectrum is characterized by the different modes of decay of the positrons in the material. The lifetime spectra can be expressed in terms of the two major modes of positron annihilation* in the following manner:

$$n = n_1 e^{-\frac{t}{\tau_1}} + n_2 e^{-\frac{t}{\tau_2}} + b \qquad (4)$$

where

n	total counts in a channel on right-hand side of zero time
n_1, n_2	extrapolated zero-time intercepts for two components
τ_1, τ_2	lifetimes of two modes of decay of positrons
t	counting time
b	constant chance coincidence background count

The first term in equation (4) includes free positron and parapositronium decays, and the second term defines the orthopositronium decays mediated by the free electrons. The orthopositronium decay component is characterized by its long life τ_2 and corresponding intensity I_2,[†] which is defined by

$$I_2 = \frac{n_2 e^{-\frac{t}{\tau_2}}}{n_1 e^{-\frac{t}{\tau_1}} + n_2 e^{-\frac{t}{\tau_2}}}$$

---

* The lifetime spectra can be resolved into more than two components. The deconvolution into two components, however, resulted in consistently better fits to the exponential data. It was therefore decided that the results can be best described by a two-component analysis.

† As indicated previously, τ_2 (and hence I_2) may be composite of several undissolved long lifetime decay components of orthopositronium atoms.

The values of τ_2 and I_2 provide useful information about the electron environment at the Ps site. A high free-electron density is expected to reduce τ_2 and I_2 and vice versa.

Positron lifetime measurements in samples containing 1:10 molar fractions of Co(acac)$_2$ and Co(acac)$_3$ complexes were measured using a standard fast-slow coincidence system described in reference 7. The coincidence system had a time resolution (FWHM) of 400 picoseconds for the Co^{60} prompt spectrum measured with Na^{22} energy windows. Figure 3 is a schematic of the positron lifetime measurement system. The lifetime spectra were acquired over a period of 12 hours for good statistics and were fitted to two component lifetimes for a good variance. Figure 4 shows a typical positron lifetime spectrum.

Combining the data summarized in tables II and V, the following general conclusions can be drawn:

1. The Co^{2+} ions increase the saturation moisture content of the MY-720 epoxy by about 21 ± 2 percent. Presumably, this results from the creation of more chemical sites for water molecule absorption or increased free volume.

2. The Co^{2+} ions reduce the probability of positronium Ps formation by about 21 ± 4 percent. They also reduce the long component lifetime τ_2 slightly.

3. The effect of Co^{3+} ions on saturation moisture content is much less than that of Co^{2+} ions. This implies that fewer additional functional groups are created by Co^{3+} ions and/or that there is a lesser increase in free volume.

4. Consistent with item (3), Co^{3+} ions also reduce the probability of positronium atom formation by a slightly smaller amount (about 14 ± 5 percent). The effect on the long component lifetime τ_2 is somewhat larger, presumably because of a better overlap between the spin-unpaired electrons centered at the impurity ions and Ps atoms.

Discussion

Epoxy structures usually have both physical and chemical[‡] sites where water molecules may enter in or bind to them. Metal ions can enhance or deter chemical entry by interacting with water molecule absorption sites in the epoxy chain. It appears that both Co^{2+} and Co^{3+} ions increase saturation moisture content in MY-720 (i.e., they possibly increase the number of functional groups where water molecules may attach to the polymer chain), though the effect of Co^{2+} ions is more pronounced. The presence of free electrons at these sites may also be expected to reduce the probability of positronium (Ps) formation, which is usually evidenced by the reduction in long component intensity I_2. These free electrons may also be expected to reduce the Ps lifetime by providing more interacting electrons near the Ps atoms. All these conclusions are generally supported by experimental data which show the effects of Co^{2+} and Co^{3+} ions on long component lifetime τ_2 and intensity I_2 values. (See table V.) These results are also in general agreement with the direct magnetic measurements of the epoxies containing Co^{2+} and Co^{3+}. These direct magnetic measurements, however, are in disagreement with what might be expected on the basis of the Ligand field theory of electronic configurations for individual ions. (See refs. 8 and 9.) The orbital motion of electrons in transition metal compounds is severely restricted by the less than spherically symmetrical environments. Consequently, one can usually neglect all but the spin contribution to the magnetic moment of the transition metal ions. Thus, a Co^{2+}(3d^7) ion is expected to have a magnetic moment of 1.73μ_0 in an octahedral (d^{2}sp^3) field and 3.87μ_0 in a tetrahedral (sp^3) field, whereas a Co^{3+}(3d^6) ion is expected to have a zero magnetic moment in an octahedral field and 4.90μ_0 in a tetrahedral field.[§] (See table VI for various electronic configurations.) Obviously, the experimental data do not agree with these predictions. The average measured value of Co^{2+} magnetic moment is (4.32 ± 0.32)μ_0, which is considerably higher than the maximum spin-only value of 3.87μ_0. Similarly, the Co^{3+} ion average magnetic moment value of (4.94 ± 0.48)μ_0 is much higher than the predicted spin-only value of zero. The spin-only expected value of 4.90μ_0 for an outer complex octahedral field, on the other hand, is in good agreement with the measured value. However, the experimental values for Co^{3+} ions range from 3.94μ_0 to 6.32μ_0, which indicates a strong possibility of an orbital contribution as well as hybridized symmetries.

The experimental data for Co^{2+} and Co^{3+} ions in MY-720 epoxy present a rather complex

---

[‡] During the curing of epoxies, hydroxyl and secondary and tertiary amines are formed. Residual epoxide and primary amines are also present. All these functional groups are believed to be responsible for water absorption via hydrogen bond formation. Water can also act with epoxide groups to form additional hydroxyl groups.

[§] Divalent cobalt forms numerous complexes of various stereochemical types of which the octahedral and the tetrahedral are the most common. The Co^{2+} ions have more tetrahedral complex than any other transition metal ions. The Co^{3+} ions, however, are formed mostly in octahedral interstices. (See ref. 10.)

behavior.** The coordinations of the two ions are complex mixtures of hybridized symmetries. Also, the orbital contributions to the magnetic moment are significant for both ions. Bivalent cobalt ions have been reported (refs. 11 through 14) to have magnetic moments greater than the value predicted for an electron spin of 3/2, namely $\bar{\mu}_{eff} = 3.87\mu_0$. Some orbital component seems to be conserved, with the degree of conservation depending on the symmetry of the environment of the magnetic ion. However, such conclusions have not been reported for Co^{3+} ions. For example, $(CoF_6)^{3-}$ has a magnetic moment indicative of four spin-unpaired electrons only, which is expected for a tetrahedral or an octahedral outer complex symmetry. (See ref. 9.) As indicated previously, however, our measured values range from $3.94\mu_0$ to $6.32\mu_0$, which indicates the possibility of a certain orbital contribution as well as hybridized symmetry.

Even though there seems to be a rather large spread in our values of cobalt ion magnetic moments (mainly due to nonuniform distribution of the cobalt ions in the host epoxy), it can generally be concluded that the cobalt ions in epoxies provide extra unpaired electrons, which may explain the beneficial effects of the $Co(acac)_3$ complex on the mechanical properties of MY-720 epoxy. However, this conclusion fails to explain why $Co(acac)_2$, which provides a roughly comparable number of spin-unpaired electrons, does not produce similar effects. The explanation may lie in the possibility that Co^{2+} ions form more antibonding or nonbonding orbitals, which therefore result in a somewhat less cohesive structure with a larger physical free volume in the specimens. A less cohesive structure may be expected to be weaker, in agreement with the data reported in reference 2. In the preceding discussion, it has been assumed that the cobalt ions in the $Co(acac)_2$-epoxy specimens have an oxidation state of 2^+, whereas cobalt ions in $Co(acac)_3$-epoxy specimens have an oxidation state of 3^+. No experimental measurements were made to confirm these assumptions. It is entirely possible that both types of specimens have mixed oxidation states and that they are mixed in different ratios in the two types of specimens. However, the data as a whole are consistent with the explicit assumptions of unique states of oxidation of the cobalt ions in respective samples and that Co^{2+} ions form more

antibonding or nonbonding orbitals than the Co^{3+} ions in the host epoxy.

Concluding Remarks

We have investigated the effects of Co^{2+} and Co^{3+} ions on selected physical properties of the MY-720 epoxy. It appears that Co^{2+} ions form antibonding or nonbonding orbitals which increase the free volume and also reduce the cohesiveness of the host epoxy. This reduced cohesiveness may account for its structural weakening when $Co(acac)_2$ is added to it. The effects of Co^{3+} ions, on the other hand, seem to result in increased cohesiveness of the epoxy with resultant improvement in its mechanical properties. The experimental values of magnetic moments of both types of ions suggest that their orbital contributions are partially conserved, though the effect is more pronounced for Co^{2+} ions. Also, their coordination symmetries do not appear to be uniquely defined. These results indicate that the effects of metal ions on resin properties cannot be easily predicted based on Ligand field theory arguments alone. Complex interactions between metal ions and the host epoxy molecular structure suggest the desirability of parallel experimental investigations of electronic, magnetic, and mechanical properties of metal ion-containing epoxy samples for comparison with the theory.

References

1. Stoakley, Diane M.; and St. Clair, Anne K.: *Metal Ion-Containing Epoxies.* NASA TM-84567, 1982.
2. Stoakley, D. M.; and St. Clair, A. K.: The Effect of Cobalt Complex Addition on the Cure and Properties of an Epoxy Matrix Resin. *J. Appl. Polym. Sci.,* vol. 31, 1986, pp. 225–236.
3. Singh, Jag J.; Holt, William H.; and Mock, Willis, Jr.: Moisture Dependence of Positron Annihilation Rates in Molecular Substances. *Nucl. Instrum. & Methods,* vol. 201, no. 2-3, Oct. 15, 1982, pp. 485–489.
4. Singh, Jag. J.; St. Clair, Terry L.; Holt, William H.; and Mock, W., Jr.: *An Investigation of Molecular Structure of Copolymers Using Positron Annihilation Spectroscopy.* NASA TM-86431, 1985.
5. Zijlstra, H.: *Experimental Methods in Magnetism.* North-Holland Publ. Co., 1967.
6. Bates, Leslie F.: *Modern Magnetism,* Third ed. Cambridge Univ. Press, 1951.
7. Singh, Jag J.; Holt, William H.; and Mock, Willis, Jr.: *Moisture Determination in Composite Materials Using Positron Lifetime Technique.* NASA TP-1681, 1980.

** It is interesting to speculate that the final oxidation state of Co^{x+} ions in the host epoxy is the same, namely 2^+. The differences in the effects of Co^{2+} and Co^{3+} complexes on MY-720 epoxy resin properties may well be the result of intermediate by-products of the $Co^{3+} \rightarrow Co^{2+}$ conversion process.

8. Orgel, Leslie E.: *An Introduction to Transition-Metal Chemistry—Ligand-Field Theory.* John Wiley & Sons Inc., c.1966.

9. Mortimer, Charles, E.: *Chemistry—A Conceptual Approach,* Fourth ed. D. Van Nostrand Co., 1979.

0. Cotton, F. Albert; and Wilkinson, Geoffrey: *Advanced Inorganic Chemistry—A Comprehensive Text,* Second rev. and augmented ed. Interscience Publ., c.1966.

1. Nakamura, Tetsuro; Arisawa, Yoshikazu; and Sata, Toshiyuki: Magnetic Moment of Co^{2+} Ion in Fused Chloride System $CoCl_2$-NaCl. *J. Phys. Soc. Japan,* vol. 28, no. 5, May 1970, p. 1370.

12. Janakirama-Rao, Bh. V.: Anomalous Magnetic Moments of the 3D Orbital Transition Metal Ions in Glass. *J. Sci. & Ind. Res.,* vol. 33, no. 3, 1974, pp. 114-119.

13. Berretz, Manfred; and Holt, Smith L.: Magnetic Properties of Some Transition Metal Ions in Barium Phosphate Glass. *J. American Ceram. Soc.,* vol. 61, no. 3-4, Mar.-Apr. 1978, pp. 136–139.

14. Baiocchi, E.; Montenero, A.; Bettinelli, M.; and Sotgiu, A.: Optical and Magnetic Properties of First-Row Transition Metal Ions in Lead Silicate Glass. *J. Non-Cryst. Solids,* vol. 46, no. 2, 1981, pp. 203–215.

Table I. Summary of Composition of Co^{3+} and Co^2 Containing MY-720/DDS Samples

Sample	Amount of MY-720/DDS/MEK solution, grams	$Co(acac)_x$, grams	Calculated percent Co^{x+}, in cured discs	Nominal metal complex mole ratio in sample[1]
Samples containing Co^{3+}				
1	7.00/1.98/9.00	0.118	0.215	1:50
2	7.00/1.98/9.00	.237	.426	1:25
3	7.00/1.98/9.00	.592	1.025	1:10
Samples containing Co^{2+}				
1	7.00/1.98/5.38	0.086	0.218	1:50
2	7.00/1.98/5.38	.171	.429	1:25
3	7.00/1.98/5.38	.428	1.044	1:10

[1] Based on repeat unit average molecular weight of 422 atomic mass units.

Table II. Summary of Saturation Moisture Contents of Samples Containing Co^{2+}/Co^{3+} Metal Ions

Sample	Metal complex mole fraction	Saturation moisture content, weight percent
Samples containing Co^{3+}		
1	Zero (i.e., reference)	4.43 ± 0.03
2	1:50	4.39 ± 0.03
3	1:25	4.48 ± 0.09
4	1:10	4.70 ± 0.03
Samples containing Co^{2+}		
1	Zero (i.e., reference)	4.43 ± 0.03
2	1:50	4.97 ± 0.12
3	1:25	4.94 ± 0.06
4	1:10	5.36 ± 0.05

Table III. Summary of β values

Field, kilograuss	β for Ni(en)$_3$S$_2$O$_3$	β for Hg[Co(SCN)$_4$]	Average
4	1.014×10^{-3}	1.018×10^{-3}	1.016×10^{-3}
6	4.713×10^{-4}	4.725×10^{-4}	4.719×10^{-4}
8	2.825×10^{-4}	2.831×10^{-4}	2.828×10^{-4}
10	2.021×10^{-4}	2.025×10^{-4}	2.023×10^{-4}

Table IV. Summary of Effective Magnetic Moments of Co^{2+} and Co^{3+} Ions in Various Test Samples

Metal complex[a] Co(acac)$_x$	$\bar{\mu}_{\text{eff}}$ of Co^{x+} in complex, μ_0	Mole fraction of metal complex in epoxy	$\bar{\mu}_{\text{eff}}$ of Co^{x+} in epoxy, μ_0
Co(acac)$_2$	$(4.76 \pm 0.01)^{[b]}$	1:50	4.42 ± 0.46
		1:25	4.96 ± 0.70
		1:10	$\begin{bmatrix} 3.54 \pm 0.87 \\ (3.59 \pm 0.05)^{[c]} \end{bmatrix}$
Average $\bar{\mu}_{\text{eff}}$ for Co^{2+} in MY-720/DDS			(4.32 ± 0.32)
Co(acac)$_3$	$(0.31 \pm 0.02)^{[d]}$	1:50	6.32 ± 0.60
		1:25	3.94 ± 1.28
		1:10	$\begin{bmatrix} 4.22 \pm 0.54 \\ (4.91 \pm 0.04)^{[c]} \end{bmatrix}$
Average $\bar{\mu}_{\text{eff}}$ for Co^{3+} in MY-720/DDS			(4.94 ± 0.48)

[a]These metal complexes were quoted as 99 percent pure by the commercial supplier.

[b]Co^{2+} ions in tetrahedral symmetry are expected to have a spin-only magnetic moment of $3.87\mu_0$. The higher experimental value suggests partial orbital contribution.

[c]These measurements were made on a separate set of samples at a different time but the samples were prepared according to the same prescription as the first set.

[d]Co^{3+} ions in octahedral (d^{2}sp^3) symmetry are expected to be diamagnetic. The experimentally observed nonzero magnetic moment implies a modified octahedral (sp^{3}d^2) symmetry as well as a slight orbital contribution resulting from internal field distortion.

Table V. Summary of Positron Annihilation Characteristics in Co(acac)$_x$ Modified Epoxy Samples

Metal complex	Mole fraction of metal complex	Average values of positron lifetimes and intensities		
		τ_1, picoseconds	τ_2, picoseconds	I_2, percent
Zero (reference)	0	386 ± 9	1737 ± 54	25.9 ± 1.9
Co(acac)$_2$	1:10	378 ± 5	1616 ± 30	20.5 ± 1.0
Co(acac)$_3$	1:10	374 ± 6	1583 ± 44	22.2 ± 1.0

Table VI. Arrangement of Electrons in High-Spin and Low-Spin Octahedral Complexes

Metal ion	High-spin state, outer complex octahedral[1] (weak Ligand field)	Low-spin state, inner complex octahedral (strong Ligand field)
Co^{3+}(3d^6)	3d 4s 4p 4d (sp^{3}d^2) 4 electrons (spin-unpaired) (^{5}D) $\bar{u}_{\text{eff}} = 4.90\mu_0$ to $5.48\mu_0$	3d 4s 4p 4d (d^{2}sp^3) 0 electrons (spin-unpaired) (^{1}S) $\bar{\mu}_{\text{eff}} = 0$ (Diamagnetic)
Co^{2+}(3d^7)	(sp^{3}d^2) 3 electrons (spin-unpaired) (^{4}F) $\bar{\mu}_{\text{eff}} = 387\mu_0$ to $5.20\mu_0$	(d^{2}sp^3)(4d^1) 1 electron (spin-unpaired) (^{2}D) $\bar{\mu}_{\text{eff}} = 1.73\mu_0$ to $3.00\mu_0$

[1]Outer complex octahedral (sp^{3}d^2) = Tetrahedral (sp^3). That is, both predict the same number of spin-unpaired electrons.
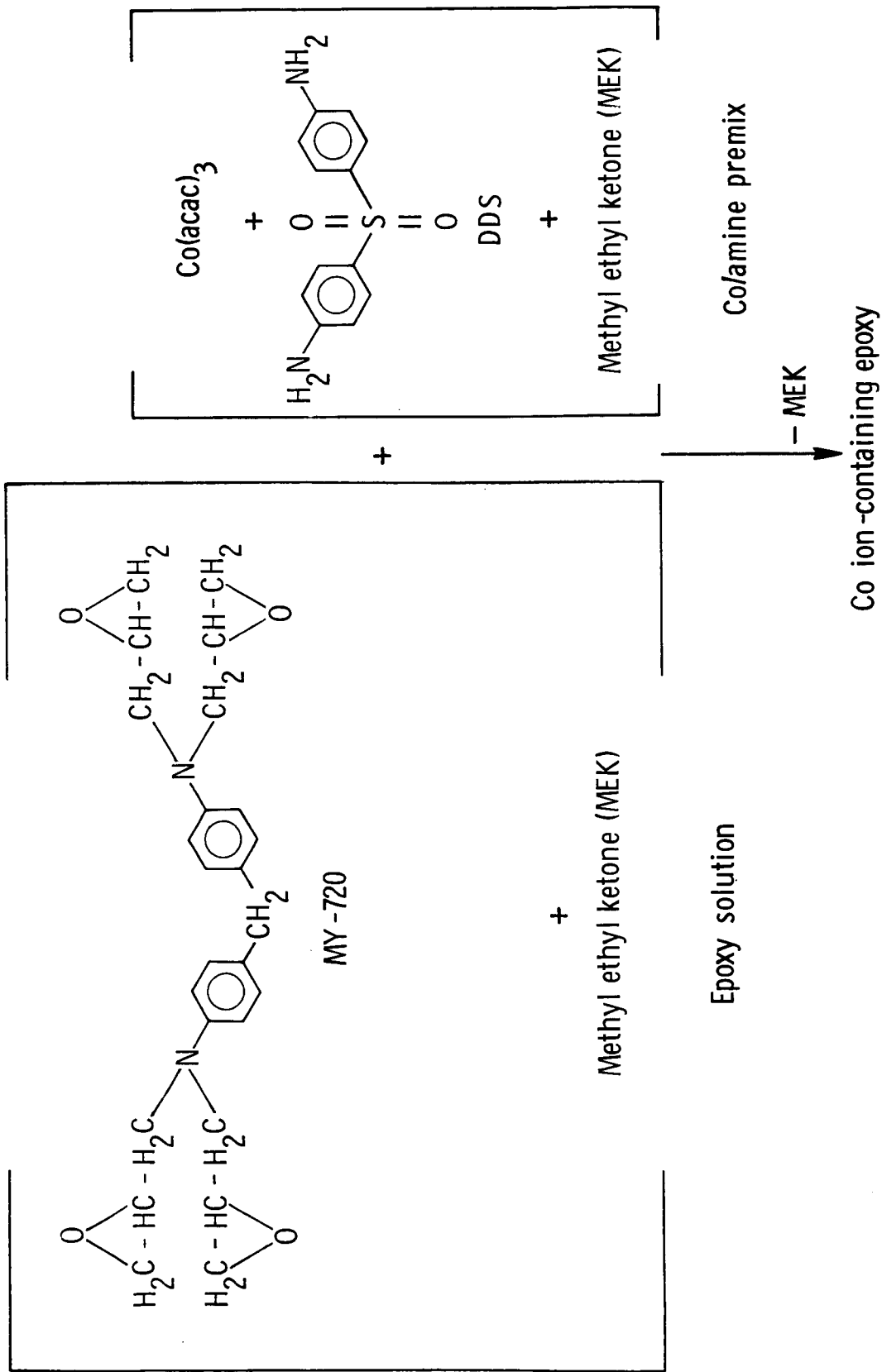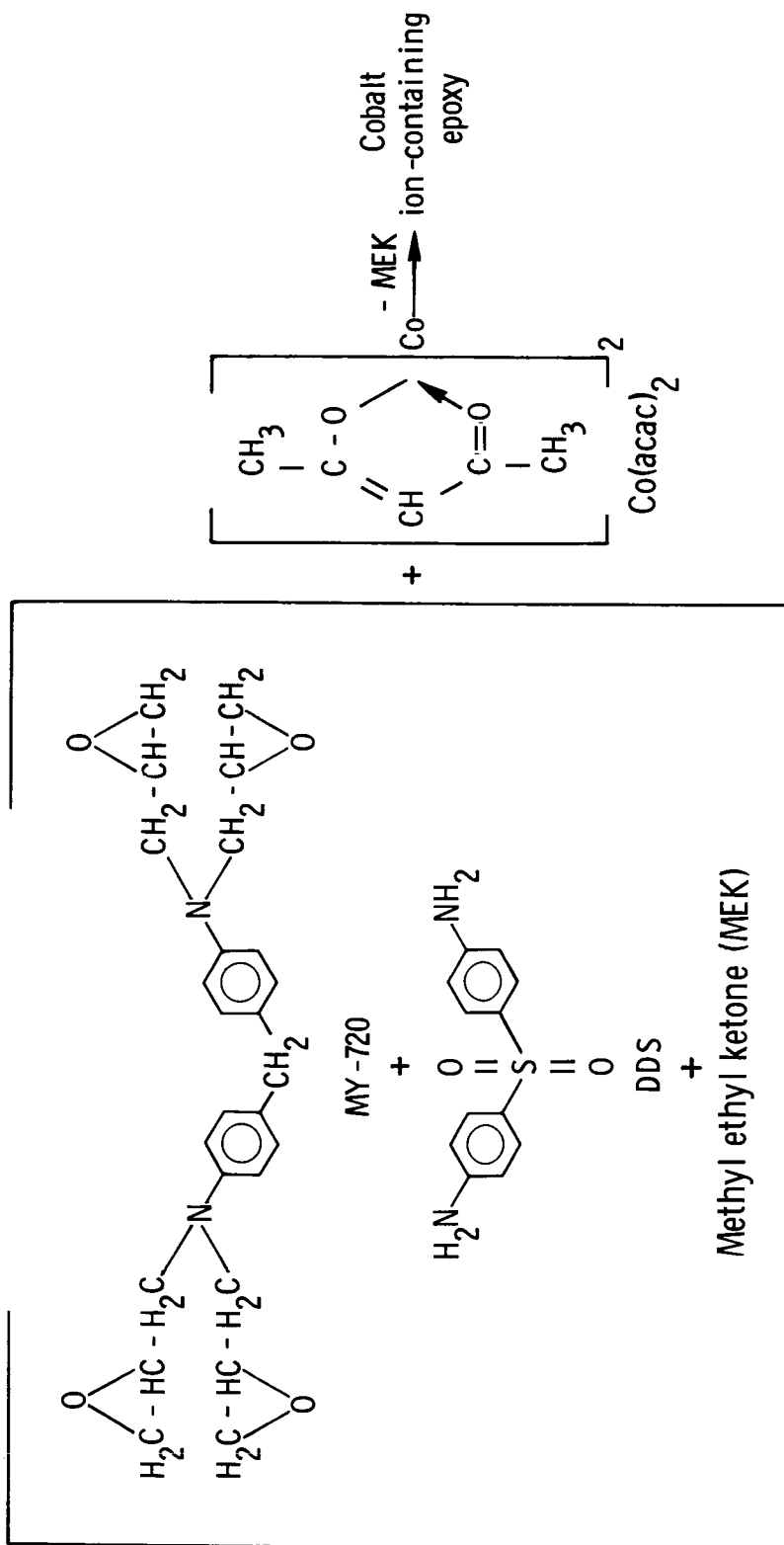
Figure 1. Premix method of preparing Co(acac)$_3$ epoxies.

Epoxy solution

$+$

Co(acac)$_2$

$\xrightarrow{\text{- MEK}}$ Cobalt ion-containing epoxy

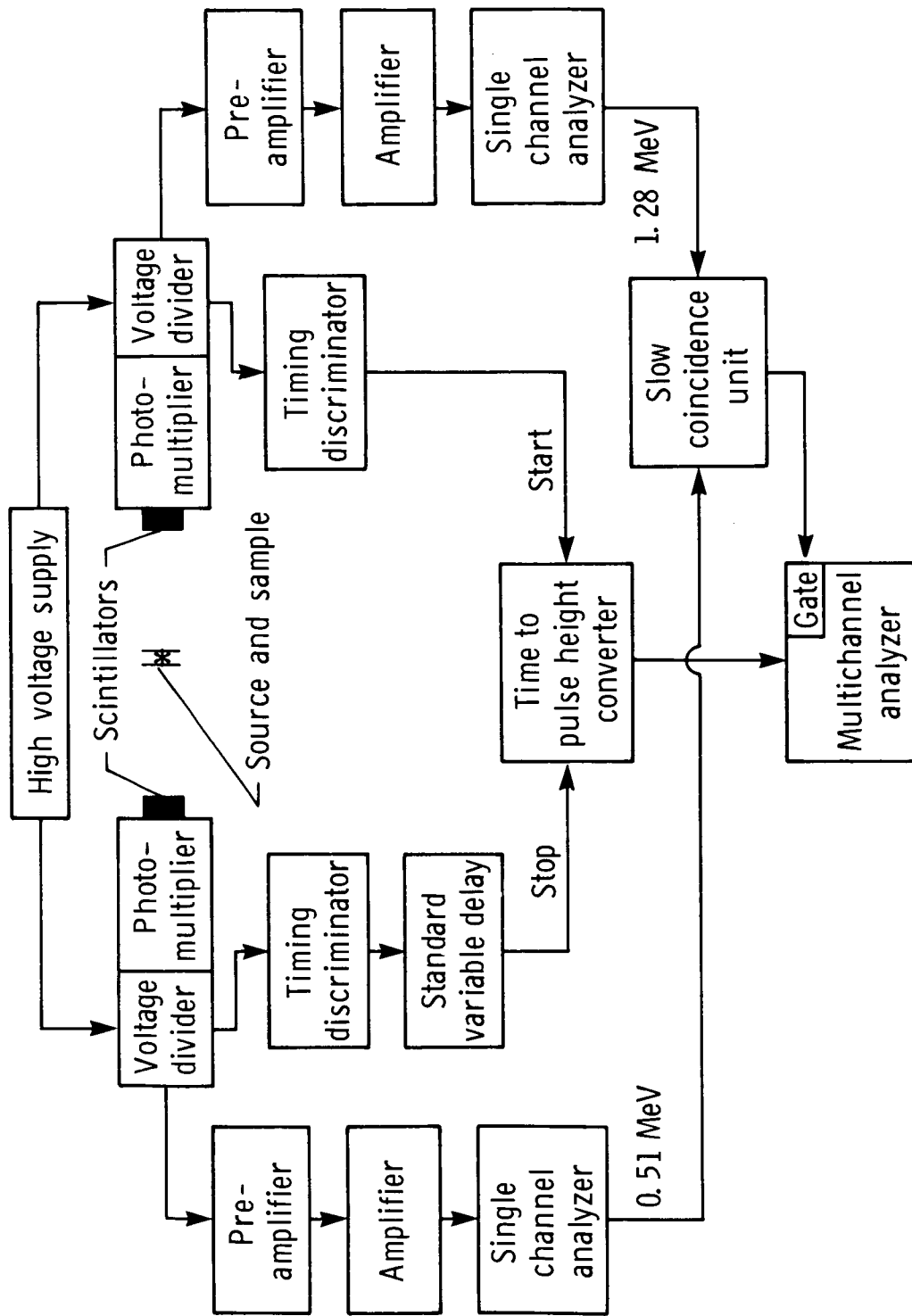Figure 2. Standard method of preparing Co(acac)$_2$ epoxies.

11

Figure 3. Fast-slow coincidence system for measuring positron lifetime spectra.
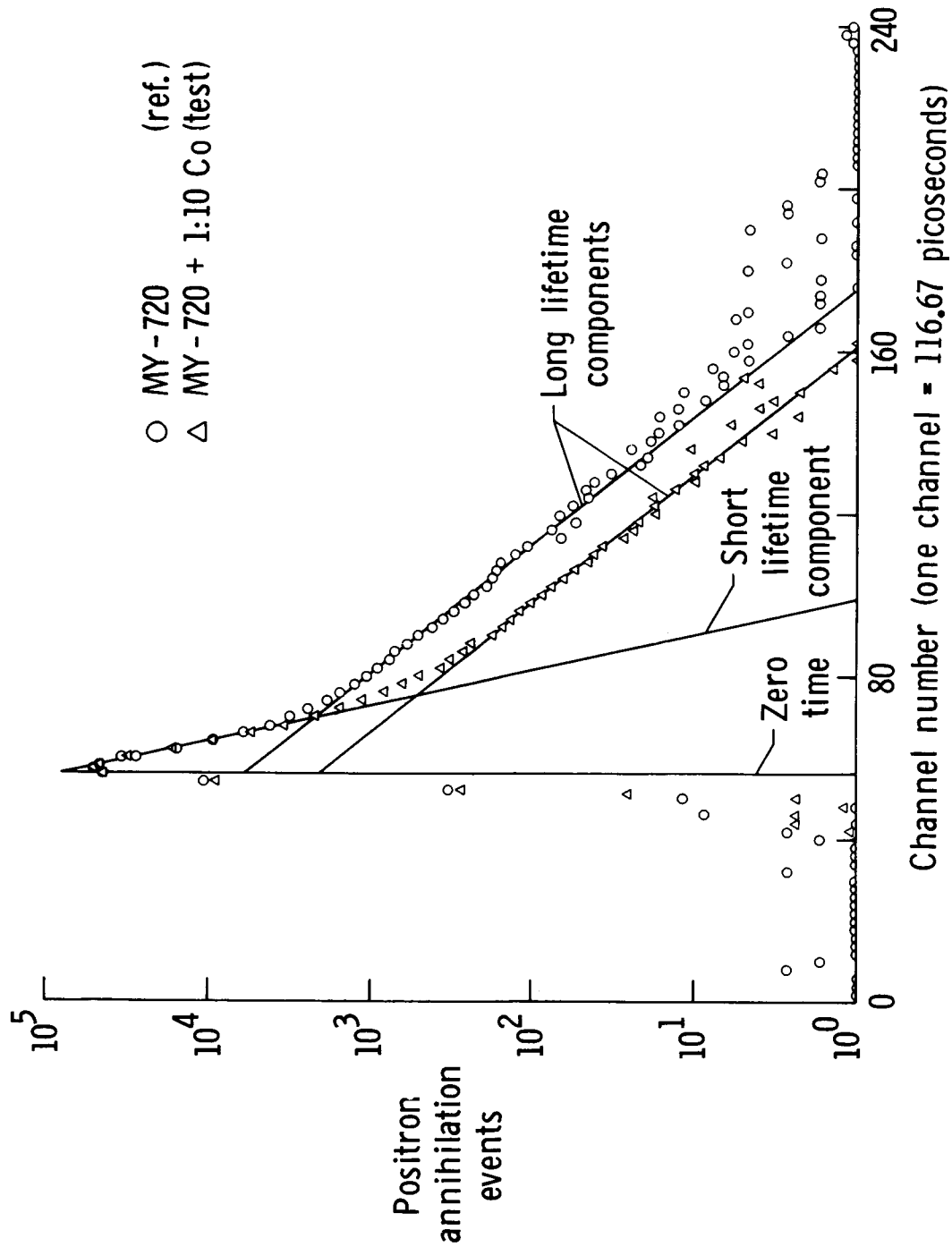
Figure 4. Typical positron lifetime spectra in test samples.

Standard Bibliographic Page

1. Report No. NASA TP-2639	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle Investigation of the Effects of Cobalt Ions on Epoxy Properties		5. Report Date December 1986
		6. Performing Organization Code 505-63-91-01
7. Author(s) Jag J. Singh and Diane M. Stoakley		8. Performing Organization Report No. L-16196
9. Performing Organization Name and Address NASA Langley Research Center Hampton, VA 23665-5225		10. Work Unit No.
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, DC 20546-0001		13. Type of Report and Period Covered Technical Paper
		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The effects of $Co(acac)_x$ complexes on MY-720 epoxy properties have been investigated. It appears that Co^{2+} ions form antibonding or nonbonding orbitals which increase the free volume and also reduce the cohesiveness of the host epoxy. The effects of Co^{3+} ions, on the other hand, seem to result in increased cohesiveness of the epoxy. The experimental values of magnetic moments of both types of ions in MY-720 suggest that the orbital momentum contributions of the (3d) electrons are partially conserved, though the effect is more pronounced for Co^{2+} ions. The coordination environment of the cobalt ions in the host epoxy does not appear to be uniquely defined. These results indicate that the effects of metal ions on resin properties cannot be easily predicted on the basis of Ligand field theory arguments alone. Complex interactions between metal ions and host epoxy molecular structure suggest the desirability of parallel experimental investigations of electronic, magnetic, and mechanical properties of metal ion-containing epoxy samples for comparison with theory.

17. Key Words (Suggested by Authors(s)) Thermoset epoxies Transition metal ions Ligand field theory Hybridized coordination Magnetic susceptibility Positron annihilation spectroscopy Free-electron density Free volume	18. Distribution Statement Unclassified—Unlimited Subject Category 27	
19. Security Classif.(of this report) Unclassified	20. Security Classif.(of this page) Unclassified	21. No. of Pages 14 22. Price A02

NASA-Langley, 1986