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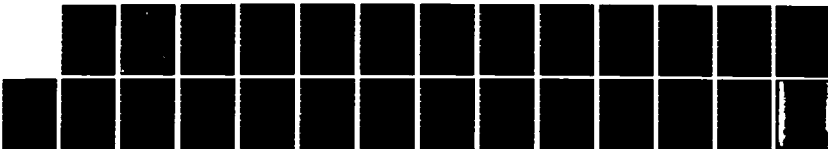
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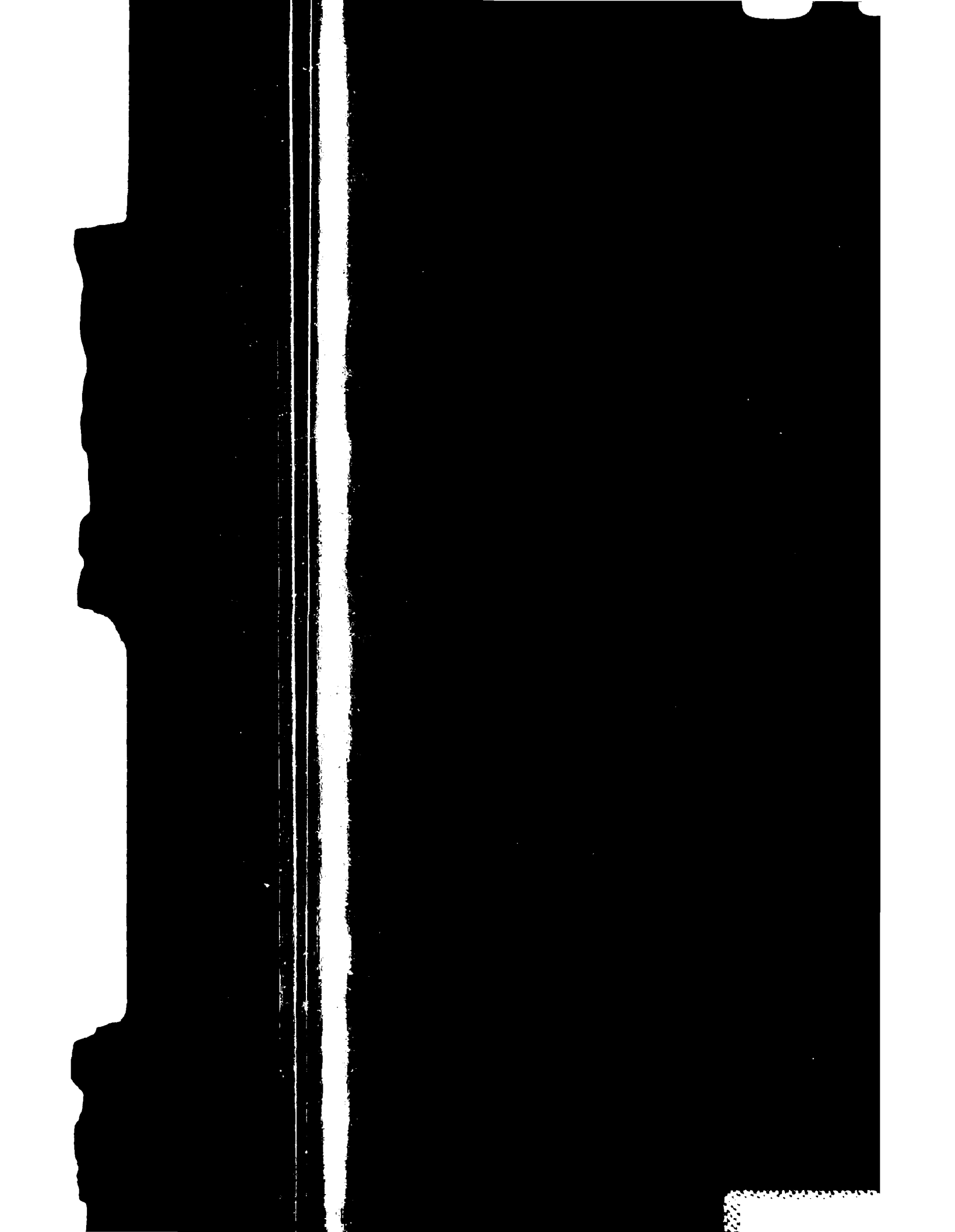
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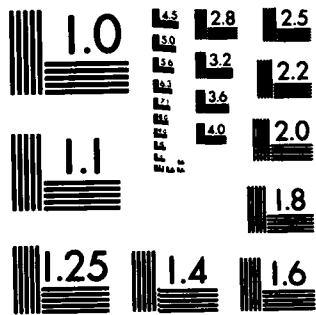
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MATERIALS RESEARCH LABORATORIES

MELBOURNE, VICTORIA

REPORT

MRL-R-657

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**INTERACTIONS BETWEEN F-111 FUSELAGE FUEL TANK SEALANTS. PART I
CHARACTERISATION OF POLYESTER SEALANTS AND THEIR
HYDROLYTIC DEGRADATION PRODUCTS**

P.J. Hanhela and D.B. Paul

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MATERIALS RESEARCH LABORATORIES

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Interactions between polysulfides and the hydrolysis products of polyester sealants EC 5106 and EC 5146 within integral fuselage fuel tanks of F-111 aircraft lead to fuel leaks. To assist in determining the mechanisms involved in this process a study of the physical changes which occur during contact of typical polysulfides with actual and model polyester products is to be undertaken. Prior to this investigation a detailed analysis of the polyester sealants was necessary to assist selection of model degradation products.

Exhaustive degradation of the polyester resins using the transesterification reagent of lithium methoxide in methanol provided suitable samples for analysis by gc/ms and other spectroscopic techniques. Major components were shown to be sebacic acid and neopentyl glycol. The most significant difference between the two polyester prepolymers was in the larger proportion of trihydric alcohol in EC 5146 which would result in a greater degree of crosslinking of this sealant compared with EC 5106. In both sealants the filler had substantially the same composition with titanium dioxide being the main component. Molecular weights and acid equivalent weights of the prepolymers, their hydrolysis products and hydrolysed cured sealants were determined to assess extent of degradation.

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HYDROLYTIC DEGRADATION PRODUCTS

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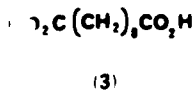
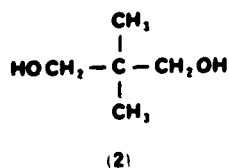
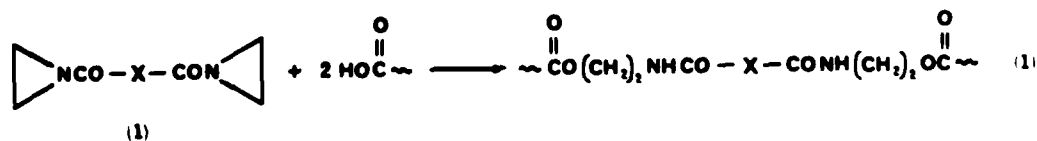
1. INTRODUCTION

In the F-111 aircraft, the original sealants were two part polyester materials which were used in a general purpose role throughout the structure. In addition, for sealing of the integral fuselage fuel tanks a multiple barrier concept was introduced. In this process a polyester sealant was applied in faying surfaces and voids, and the fasteners and seams which were in direct contact with fuel were sealed with fillets of polysulfide. The susceptibility of the polyester sealants to hydrolysis in humid environments, however, led to their degradative collapse and severe fuel leaks eventuated.

The gross composition of the polyesters [1] and the kinetics of the hydrolysis process [2] have been examined briefly to define the chemical nature of the problem and to assist in developing a practical repair procedure. The subsequent refurbishment of the fuel tanks has been described in detail [3] and only pertinent features are considered here. Hydrolytic degradation results in the polyester sealant changing from a firm elastomer to a viscous gum. Within the fuel tank structure the polyester and polysulfide sealants are adjacent and eventually the mobile polyester degradation products contact the polysulfide material. It is considered that a combination of the pressure which arises from expansion during polyester hydrolysis and the chemical effect of the degradation materials on the polysulfide cause the fillet seal to rupture and create a fuel leak [4]. As it is impractical to remove the polyester from the fuel tank faying surfaces the repair procedure is based on the introduction of a chemically resistant, flexible barrier of epoxy adhesive between the polyester and polysulfide to prevent contact between the sealants [3-5]. To allow the application of the epoxy coat the original polysulfide fillet seals must first be removed by use of a hot solution of thiphenol as the desealing agent [6]. After application of the barrier coat the tanks are resealed with a polysulfide of improved thermal stability which meets the requirements of a revised specification, MIL-S-83430.

While this repair procedure restores the fuel tanks to a condition approximating to that originally demanded it would be unreasonable to expect that they will remain viable over the long term. It is therefore essential that any revised reseal programme be based on a comprehensive understanding of the interactions between the polysulfide sealant and polyester hydrolysis products which lead to failure of the fillet seals. A knowledge of the chemical structures of the polyester degradation fragments is consequently fundamental to such an investigation. General types of polyester resins suitable for formulating sealant compositions have been described in the patent literature. Such polyesters are normally derived from dibasic aliphatic acids and dihydric alcohols and are cured with *N, N*-bis(1,2-alkylenamides) (1) as shown in equation 1. Since hydroxyl groups usually are insufficiently reactive to participate in such crosslinking processes, the polyester polymers contain free carboxylic acid groups as terminals. Chain branching and crosslinking sites may be introduced by judicious addition of polyhydric alcohols, polybasic acids or polyanhydrides [7].

Two polyester sealants were used for sealing the F-111 fuel tank structures. The initial material, designated as EC 5106, was superseded by a modified product EC 5146 which, although less susceptible to hydrolysis, also degraded in service [2]. In an earlier study evidence was presented indicating that the curing agents for both polyesters were identical and of the *N, N'*-bis(1,2-alkenamide) type [1]. Although the structure was not established in detail, available data suggested that it was based on a branched C_7H_{14} unit (1; $X = C_7H_{14}$). The polyester prepolymers, designated respectively as EC 5106B and EC 5146B, were considered to be derived principally from neopentyl glycol (2,2-dimethyl-1,3-propanediol) (2) and sebacic acid (octanedioic acid) (3). The differences between the two sealants were attributed to different proportions of maleic acid which were suggested to be present in the prepolymers. In the present study, however, inspection of the pmr spectrum of the prepolymer EC 5106B revealed no signals attributable to the methine protons of maleic acid units. As a consequence the structure assignments have been reinvestigated.



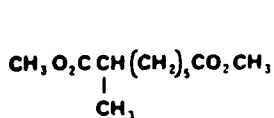
2. RESULTS AND DISCUSSION

The general approach used to identify the components of the polyester sealants involved degradation of the prepolymers EC 5106B and EC 5146B to mixtures of fragment molecules and subsequent examination using spectroscopic means. Appropriate analytical samples were obtained through exhaustive degradation and transesterification of the prepolymers with lithium methoxide in methanol, followed by acetylation of the resulting alcohols. An initial gc investigation established conditions and columns which allowed satisfactory separation of components and from retention time comparisons a preliminary screening of candidate compounds was possible. Subsequent examination of these samples using gc/ms analysis permitted assignment of structures to components of the mixture. Relevant chromatographs and the peak assignments are shown in figs. 1 and 2. The major components of the polyester were confirmed to be neopentyl alcohol (2) and sebacic acid (3). All but one of the other dibasic acids were identified as homologues of sebacic acid which presumably are present in the commercial material. The remaining dibasic acid although present in both polymers, was more abundant in EC 5106B. The base peak of its dimethyl ester appeared at m/e 185 and the remainder of the spectrum showed a close correlation with that of dimethyl sebacate. As the dimethyl esters all give a base peak of M-31 it is concluded that the diester has a molecular weight of 216. The spectrum, however, does not correspond to that of dimethyl nonanedioate [8], the simplest aliphatic dibasic acid ester of this molecular weight. A branched derivative is therefore likely with the branching occurring near the end of the chain to allow the spectral similarity to dimethyl sebacate. Dimethyl 2-methyloctanedioate (4) is therefore suggested as a possible structure. This material also exhibited a broad gc peak and although this would normally be interpreted as an indication of polar character, the pretreatment of the mixture would render this unlikely. Another unusual feature of the compound concerned the sensitivity of its peak intensity to the conditions of the gc analysis.

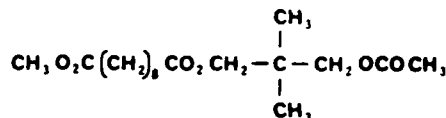
Both the EC 5106B and EC 5146B prepolymer mixtures showed the presence of small quantities of various di- and tri-hydric alcohols in addition to neopentyl glycol. Some of these compounds may have been introduced as artefacts in commercial samples. An unidentified compound in the EC 5146B mixture had a short retention time and showed ions at m/e 73 (weak), 56 and 43 which indicated an acetate derivative that fragments to a C_3H_4O or C_4H_8 unit. Butyl acetate was eliminated through retention time comparisons but the diacetates of propylene or trimethylene glycols remained as possibilities. Additional evidence for the participation of alcohols other than neopentyl glycol was obtained through the isolation of a small yield of relatively insoluble material from the EC 5106B prepolymer. The pmr spectrum of this compound was consistent with a polyester based on sebacic acid and diethylene glycol.

The compound with longest retention time is considered to result from incomplete degradation of the polyester and is ascribed as the monoester (5) of sebacic acid and neopentyl alcohol which has been partially transesterified and subsequently acetylated. This structural assignment is supported by the mass spectrum of (5) which shows fragment ions at m/e 313 (M-31) and 199 ($CH_3CO_2(CH_2)_8CO$) and a prominent ion at m/e 43 (CH_2CO)

characteristic of acetate derivatives.



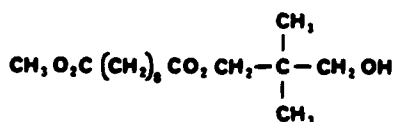
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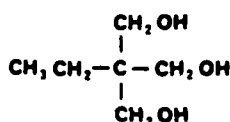
(5)

No evidence for the presence of tri- or poly-basic acids in the polyesters was obtained by this analytical approach. If polycarboxylic acids were present as chain branchers, complete esterification would be needed to permit detection by gc analysis. The transesterification reaction, however, would not be expected to esterify such carboxylic acid terminal groups and treatment of terephthalic acid with lithium methoxide in methanol in fact was shown to lead to almost total recovery of unreacted acid. The polyester prepolymers therefore were again submitted to the degradation process but with an esterification step added to ensure that all materials would be sufficiently volatile to pass through the gc column. No significant new products were observed and the most notable difference was the reduction in the alcohol proportions relative to the diacids (Table 1). This effect is attributed to ether formation from the alcohols caused by interaction with the sulfuric acid esterification catalyst. A modest increase in the yield of the unknown acetate was also noted in the case of EC 5106B and the peak ascribed to the ester (5) was diminished as a consequence of the extended reaction time for the lithium methoxide degradation. With EC 5146B a further peak with retention time slightly less than for (5) was observed. From its mass spectrum this material is assigned as (6) and must arise through incomplete acetylation.

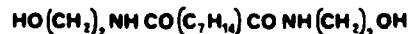
From the EC 5146B reaction mixture, a small yield of ether insoluble resin was isolated which showed a broad, ill-defined pmr band centred at 7.0 ppm, a methylene signal at 3.83 ppm and other minor aliphatic peaks. Although the infrared spectrum also supported the presence of aromatics there clearly could be no carboxyl substitution since this would produce a pmr chemical shift nearer 8.3 ppm. The ^{13}C magnetic resonance spectra reported previously [1] also showed peaks at 127.5 and 129.9 ppm which could suggest the presence of minor quantities of aromatic substrates. Pmr spectra of the degraded sealants and their prepolymers, however, indicate that these species are present in insignificant amounts (< 0.2%) and therefore the possibility of crosslinking through polyfunctional aromatic acids such as pyromellitic or trimesic acid was eliminated. The material from the EC 5146B reaction mixture is therefore considered to be derived from a compounding additive.



(6)



(7)



(8)

The area percentages of the various components of the polyester prepolymers are listed in Table 1. These indicate that the only significant chemical difference between the two lies in the degree of chain branching which results from the presence of trihydric alcohols. Examination of the pmr spectra of the materials also reflects this change. The relatively isolated peak which occurs near 3.66 ppm is attributed to the methylenes of the hydroxymethyl groups of units of trimethylolpropane (7), [9]. Integration of these peaks relative to those of the CH_2CO moiety indicates that there is 2 to 2.5 times the proportion of triol units in EC 5146B relative to EC 5106B. The prepolymer syntheses are carried out with acid in excess so therefore the branches will also be acid terminated thereby allowing crosslinking as well as chain extension.

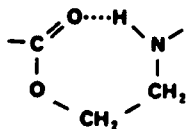
The curing reaction will produce a new aliphatic ester group and introduce amide functions (equation 1). Subsequent hydrolytic degradation at temperatures less than 100°C would not affect the amide C-N bond and consequently all cleavage will occur at the ester groups. Exhaustive hydrolysis would therefore generate sebacic acid (3), neopentyl glycol (2) and the amide (8) as the simplest fragments. In practice, however, it would be expected that polyester fragments would be produced that were terminated in hydroxyl and carboxylic acid groups and which in many cases would retain the amide moiety.

In order to obtain a measure of the degree of degradation, number average molecular weights, acid number and acid equivalent weights of the EC 5106B prepolymer, hydrolysed prepolymer and degraded sealant were determined. Vapour pressure osmometry provided number average molecular weights and acid equivalent weights were obtained by end group analysis both through pmr spectra of the resins and their methyl esters or by potentiometric titration (Table 2). Although the pmr spectra are complex the chemical shifts of the functional groups are sufficiently separated to allow interpretation. Integration of the carboxylic acid or methyl ester signals of the prepolymer or methyl esterified prepolymer against either the CH_2CO groups of neopentyl units or the CH_2CO groups of the sebacates suggests that for every CO_2H group there are 3.5 to 4 neopentyl-sebacate units. Therefore, an acid equivalent weight of around 950-1050 is indicated. Similarly, a figure for the degraded prepolymer may be obtained but the approach is unable to be applied to the degraded sealant since the spectrum will be a composite of units with and without the crosslinker attached. These results are in reasonable agreement with those obtained by titration of the carboxylic acid end groups against sodium hydroxide in an organic solvent. It is most interesting to compare the equivalent weights of our 9 year old samples to the value of 1800 obtained with fresh material [10]. Clearly a slow hydrolytic degradation has occurred in the case of the older prepolymer. Such a process not only reduces the number average molecular weight but introduces hydroxyl end groups in concert with new carboxyl groups. The relationship of $\text{MW} = 2\text{XEW}$, which is true to a first approximation in fresh prepolymer consequently cannot be used. The method does, however, provide a guide to the extent of degradation.

Close examination of the infrared spectrum of the EC 5106B resin also failed to reveal evidence of aromatic species. The CAIR difference spectrum between the hydrolysed prepolymer and the prepolymer resin indicated

the formation of a carboxylic acid at 1698 cm^{-1} (1709 cm^{-1} in chloroform) which corresponds to the frequency expected for a long chain aliphatic dibasic acid [11] (sebacic acid : 1696 , adipic acid : 1700 cm^{-1}) and indicates that considerable degradation has taken place. The difference spectrum between degraded EC 5106 sealant and the prepolymer resin shows the expected aliphatic secondary amide (1655 , 1520 cm^{-1}) in the hydrolysed sealant. The presence of the amide bands supports the premise that this group remains stable under the degradation conditions. The difference spectrum also displayed a further weak band at 1711 cm^{-1} . Interaction of a carboxylic acid with the *N,N*-bis(1,2-alkylenamide) curing agent will generate a new ester group and the frequency of such a vibration band could be subject to the effect of weak hydrogen bonding with the amide group as shown in (9). To examine this possibility the model compounds (10a,b) were prepared. The spectra of these materials showed ν_{CO} at 1740 cm^{-1} , however, and therefore the absorption at 1711 cm^{-1} is attributed to a carboxylic acid.

The degraded sealant was also examined by exploiting solubility differences between components of the mixture. Two fractions were obtained, one of which contained the bulk of the amide moiety whereas the other more closely resembled hydrolysed prepolymer. Both were esterified, separated further through differential solubilities, and the resulting fractions were studied using pmr spectroscopy. The more soluble mixtures gave spectra which were almost identical to that of methyl esterified hydrolysed prepolymer whereas the insoluble fractions showed additional broad signals assigned to the presence of NH and hydroxyl groups. This result confirmed the expectation that degradation of the sealant would generate a mixture of materials some of which would contain amide functional groups whereas others would simply be low molecular weight polyesters.



(9)



- (10) (a) $\text{R} = \text{CH}_3$
 (b) $\text{R} = (\text{CH}_2)_n\text{CH}_3$

The greater resistance [2] of EC 5146 sealant compared with that of EC 5106 could result from a number of factors. The only obvious chemical difference between the sealants is the larger proportion of trihydric alcohol in EC 5146. With both materials the degree of steric hindrance imposed by the neopentyl groups would be equivalent. The additional crosslinking that results from the extra trifunctionality in EC 5146 would, however, require the breaking of more bonds to produce fragments of the same molecular weight as those from EC 5106, and this is considered to be the major influence on degradation rates of the sealants.

The hydrolysis of fatty acid esters normally requires forcing conditions in the absence of mineral acid catalysts [12]. The rate of hydrolysis that is observed in service therefore is indicative of a catalysed process and the most likely means for this to occur would be by introduction of hydrogen chloride through the N,N-bis(1,2-alkylenamide) which is prepared from an acid chloride [7]. Other means of stabilising the polyester system could therefore involve use of acid absorbing fillers. X-Ray fluorescence and diffraction analysis showed that the principal component of the EC 5106 filler was titanium dioxide (rutile) with smaller amounts of silica and traces of aluminium and zinc compounds. Although the proportion of silica was somewhat greater in EC 5146 the major component was still titanium dioxide and no carbonates were present (Table 3). It is highly unlikely therefore that the greater hydrolytic stability of EC 5146 results from modification to the fillers. In the case of polysulfide sealants it is noteworthy that attempts to include acid absorbing fillers resulted in unpredictable changes in the cure rate [13]. Although a different cure mechanism applies with the polyesters it is conceivable that similar problems could arise if such fillers were introduced.

3. EXPERIMENTAL

3.1 General

¹H nmr spectra were recorded at 60 MHz on a Varian EM360L spectrometer using tetramethylsilane as internal reference. Mass spectra were obtained using a Vacuum Generators model 7035 instrument equipped with laminated magnet, digital scanner and Varian 3700 gas chromatograph. Operating conditions were: source temperature 200°, scan speed 0.2 sec/decade, cycle time 0.72 sec, ionising voltage 70 eV, accelerating voltage 4 Kv, split ratio 100:1 and temperature programming of 30° at 5°/minute. The gas chromatograph employed a 50 m x 0.2 mm bonded phase (BP1)-fused silica column and SGE universal injector. Preliminary gas chromatograms were provided by a Varian 3700 instrument using a 27 mm x 0.5 mm ID SCOT SP-2100 column, temperature programmed from 150° to 250° at 6°/min and monitored by a flame ionisation detector. Both injection and detector temperatures were 250°, helium flow rate was 2.5 cc/min and the sample injection volume was 0.05 or 0.1 µl. Infrared spectra were determined with a Perkin-Elmer 580B double beam ratio recording infrared spectrophotometer equipped with a model 3600 data station and associated software. Number average molecular weights were obtained with a Hewlett Packard 302B vapour pressure osmometer. X-ray fluorescence spectroscopy was carried out with a Philips model PW 1400 sequential spectrometer using compressed disc samples of 10% mixture in pure cellulose. The titanium dioxide in the sealant filler was identified as rutile by comparison with a known sample using a Philips PW 1730 high tension X-ray generator operated in the powder diffraction mode. Emission spectroscopy was performed using a 3 metre Band Atomic photographic spectrograph, model GX-1 with samples arced as a powder in a graphite cup.

3.2 Materials

(a) Sealants

Samples of 3M Company polyester sealants EC 5106 and EC 5146 were obtained through Air Office, and were cured according to manufacturer's recommendations.

(b) Polyesters

(1) EC 5106B polyester resin

The prepolymer EC 5106B B-6 (lot 21G3P) was treated with acetone and the bulk of the filler was removed by filtration. Centrifugation of the filtrate gave a clear supernatant solution which was freed from acetone to afford the polyester as a viscous oil. When exposed to sunlight for several days this clear brown resin partially solidified and a purple-brown colouration developed. The residues were washed successively with acetone, chloroform and ether, dried in air and examined by X-ray fluorescence and emission spectroscopy (see Table 3).

The ^1H nmr spectrum (CDCl_3) of the polyester showed δ 5.97 (broad, 2 x CO_2H), 3.82 (sharp line superimposed on a series of small lines from δ 3.33-4.5, 11 x CH_2O), 3.25 (s, 1 x CH_2O of trimethylolpropane units), 2.0-2.75 (m, main peaks at δ 2.15 and 2.27, 11 x CH_2CO_2), 1.0-2.0 (m, intense line at δ 1.3, 33 x CH_2 (long chain)), 0.93 (s, 8 x CH_3). The methyl signal significantly overlapped those from the long chain CH_2 groups. In CD_3SOCD_3 the carboxyl signal was absent and a broad ill-defined series of very weak bands could be discerned from δ 6.5-8.2. The remainder of the spectrum was similar to that in CDCl_3 with δ 3.80, 3.17, 1.83-2.75, 1.0-1.83 and 0.90 respectively. The neat resin had ν_{max} 2500-3650 (free and bonded hydroxyl) and 1739 cm^{-1} (ester carbonyl) with evidence of a shoulder (carboxylic acid) centred at 1710 cm^{-1} . In solution (CHCl_3) the ester band appeared at 1725 cm^{-1} .

Treatment of the polyester resin with ether gave a minor quantity of insoluble semi-solid material which was washed with acetone to produce a rubbery residue. The acetone solution was poured into water and the resulting precipitate was extracted with chloroform. Removal of the solvent gave an off-white semi-solid which had δ 6.5-7.16 (broad, 2 x CO_2H), 3.9 (t, 10 x CH_2O), 3.66 (t, 10 x CH_2O), 2.0-2.5 (m, main peaks at δ 2.33, 2.23; 10 x CH_2CO), 1.1-2.0 (m, main peak at δ 1.32; 30 x long chain CH_2). This material is assigned as the polyester $[\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCCH}_2(\text{CH}_2)_6\text{CH}_2\text{C}]_n$. Infrared spectra of the insoluble fractions were indistinguishable and were similar to that of the bulk polyester resin (ν_{max} (KBr): 1730 cm^{-1}).

(2) Hydrolysed EC 5106B polyester resin

The polyester resin EC 5106B was separated from fillers as above and then maintained at 90° and 100% relative humidity for 10 days (3% weight gain). The hydrolysed resin had δ (CDCl_3): 5.9 (broad, 2 x CO_2H), 3.5-4.66 (m, intense band at δ 3.83, 4.2 x CH_2O), 3.43 (s, 0.4 x CH_2O of trimethylolpropane units), 2.1-2.66 (m, main signals at δ 2.35 and 2.45;

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the presence of a carboxylic acid in the
(film) or 1709 cm^{-1} (CHCl_3)).

(lot 51E4P) had formed an elastomer on
the same way as EC 5106B.

at

5106 sealant were degraded at 95° and 95%
the product was extracted with
removed by centrifugation. The hydrolysed
dichloromethane solution as a viscous,
solidified on standing. Conventional
acid components were unsuccessful.
3.35-4.5 (m, intense line at 3.9), 3.33
0-2.65 (m, intense peaks at 2.08 and
0.5) and 1.0. Integrated intensities of
7:10:34:12. The degraded sealant had
shoulder) and 1645 cm^{-1} (secondary amide);
shoulder at 1705) and 1660 cm^{-1} . Difference
EC 5106B resin showed the presence of an
hydrolysed sealant, ν_{max} (CHCl_3):1658 and
Further weak bands observed at 1721
could be assigned unambiguously. Evidence
was derived from the difference spectrum of
EC 5106B resin which showed ν_{max}
1644 and 1541 cm^{-1} . Additional bands
possibly are associated with ester
in the amide crosslinking units. Each of
1710-1720 cm^{-1} region.

t

maintained for three weeks at 95° and 95%
dried filler was separated and analysed
dark semi-solid sealant degradation
intense, broad extending to 2500 cm^{-1}),
1645 and 1625 cm^{-1} and δ (CDCl_3):6.35-
5.2 (s, broad), 3.17-4.33 (m, main line
signal at 3.28), 1.92-2.66 (m, main peaks
signal with intense peak at 1.26), 0.9
e respectively 2:8:13:10:37:14.

(c) Model compounds for infrared

The N-(2-acetoxyethyl)amide
synthesised by the method of Roe, M
 ν_{max} (film):3370 (shoulder), 3285,
had ν_{max} (KBr):3285, 1740, 1713 (w),
 ν_{max}

3.3 Esterification of Polyesters

The various polyester resi
were esterified by heating the solut
catalyst for 24 h. Excess methanol
chloroform. The resulting solution
the solvent removed to afford methyl

- (a) Methyl esterified EC 5106E
(OCH_3), 3.27 (CH_2O of trim
peaks at 2.0 and 2.27 (CH_2
chain CH_2), 0.92 (CH_3).
signals were 10:5:9:1.9:10
(sharp), 3450, 3550 cm^{-1} (
the resin is inferred sinc
terminal groups.
- (b) Methyl esterified hydrolys
3.63 (s), 3.30 (s), 2.0-2.
1.08-2.0 (main peaks at 1.
ratios were 27:12:0.9:10:3
3450 (weak), 1740 cm^{-1} (sh
- (c) Methyl esterified degraded
3.67 (s), 3.3 (s), 2.0-2.6
Integration ratios were 3.
(film):3480 (weak, broad)

Water soluble glycol or alcohol degr
extracted during workup for cases (b

3.4 Separation of sealant degradati

(a) EC 5106

Extraction of degraded EC
fraction with virtually no amide mat
(film):3350, 1735, 1645 and 1545 cm^{-1}
secondary amide. The soluble fract
peak at 3.80), 1.83-2.66 (m), 1.0-1.
integrating for 1:1:1:5:1 respective
(CD_3SOCD_3):7.83 and 6.83 (weak, broa
band which peaks at 3.58 together wi
3.76), 1.83-2.66 (m), 1.0-1.83 (m, i
signals had relative integral ratios

Each of the above fractions was methyl esterified and again solvent extracted. The original ether soluble material afforded an ether soluble orange oil (minor component) which showed no amide peaks in its infrared spectrum and the pmr spectrum was identical with that of esterified hydrolysed EC 5106B resin. The chloroform soluble component of the esterification of the original ether insoluble product had only very weak amide bands and was also virtually identical with esterified hydrolysed EC 5106B. The solvent insoluble fractions of the esterified samples were both deeply coloured, showed intense amide bands in the infrared spectra and the pmr spectra were similar to that of the insoluble unesterified product with the addition of a CH_3O band at δ 3.63.

(b) EC 5146

Ether extraction of degraded EC 5146 sealant similarly gave soluble and insoluble fractions. Infrared spectra showed the soluble material to resemble that of hydrolysed polyester resin whereas the insoluble fraction had ν_{max} (film): 3400, 1740, 1645 and 1550 cm^{-1} .

3.5 Exhaustive degradation of polyesters

- (a) The elastomeric EC 5146B prepolymer (28 g) was heated under reflux with lithium methoxide in methanol (0.5 M, 500 ml) for 16 h and stirred a further 48 h at room temperature. The mixture was filtered to remove fillers (11.8 g), the filtrate neutralized ($\text{CH}_3\text{CO}_2\text{H}$) and freed from solvent. The residue was treated with acetic anhydride (30 ml), heated at 95° for 4 h and the volatiles then removed under reduced pressure. Water (250 ml) was added to dissolve lithium acetate and the mixture was extracted with dichloromethane. The extract was washed with aqueous sodium bicarbonate, dried and the solvent removed to afford a brown oil which was maintained under vacuum at 100° for 10 min to remove residual acetic anhydride.
- (b) The prepolymer EC 5106B was treated similarly.
- (c) The above degradation products were examined by gc and gc/ms. Operating conditions are described in the introduction to this section, spectra are shown in Figs. 1, 2 and results are given in Table 1. Mass spectroscopic data for these products (m/e , relative abundance) are as follows: (a) dichloromethane: 88 (6%), 86 (34), 84 (59), 51 (31), 49 (100), 47 (12); (b) neopentyl glycol diacetate: 115 (10%), 103 (8), 88 (6), 68 (8), 56 (21), 55 (6), 43 (100); (c) diethylene glycol diacetate: 117 (2%), 87 (76), 61 (3), 43 (100); (d) trimethylolpropane triacetate: 128 (7%), 86 (41), 68 (15), 43(100); (e) trimethylolethane triacetate: 86 (44%), 43 (100); (f) unassigned glycol acetate; 73 (2%), 56 (32), 43 (100) (n-butyl acetate has m/e : 73 (13%), 56 (27), 43 (100), 41 (13) and a shorter retention time); (g) dimethyl sebacate: 199 (25%), 166 (18), 157 (23), 138 (16), 137 (25), 125 (80), 98 (58), 97 (37), 87 (34), 84 (44), 83 (26), 74 (100), 69 (35), 59 (39), 55 (84), 43 (41), 41 (49); (h) dimethyl undecanedioate: 213 (21%), 171 (18), 152 (16), 139 (43), 112 (17), 111 (13), 98 (73), 97 (24), 87 (32), 84 (50), 83 (21), 74 (100), 69 (62), 59 (36), 55 (73), 43 (52), 41

(58); (i) dimethyl dodecanedioate: 227 (18%), 185 (17), 153 (25), 135 (13), 112 (25), 111 (15), 98 (85), 97 (21), 87 (37), 84 (54), 83 (28), 74 (100), 69 (59), 59 (32), 55 (70), 43 (44), 41 (56); (j) suspected dimethyl 2-methyloctanedioate: 185 (11%), 166 (10), 138 (18), 125 (23), 98 (47), 97 (14), 87 (30), 84 (32), 83 (10), 74 (100), 69 (12), 59 (13), 55 (44), 43 (30), 41 (28); (k) acetate of neopentyl sebacate monomethyl ester (5): 313 (3%), 199 (65), 139 (18), 129 (30), 128 (13), 98 (15), 97 (14), 84 (10), 69 (56), 56 (32), 55 (28), 43 (100), 41 (28).

Various model compounds were synthesised to verify gc response times prior to the gc/ms examination. Diols and trihydric alcohols were acetylated in the following manner. The diol (0.2 mole) and acetic anhydride (0.5 mole) were mixed, stood in ice-water for 0.5 h and then warmed on a steam bath for a further 0.5 h. The cooled mixture was poured into water, extracted with ether, washed (sodium bicarbonate) and dried ($MgSO_4$). Removal of the solvent afforded the diacetate which was examined by infrared spectroscopy to ensure complete acetylation had occurred. The acetates of the following alcohols were synthesised by this process: neopentyl glycol, diethylene glycol, butanol, propylene glycol, trimethylolpropane and trimethylolmethane.

Methyl esters of the following acids were prepared as reference compounds by acid catalysed esterification in methanol: sebacic acid, terephthalic acid, pyromellitic acid, maleic acid, adipic acid, azelaic acid and suberic acid.

To ensure complete esterification during the exhaustive degradation reactions, an esterification step was added after the acetylation. The nonvolatile products from (a) were taken up in methanol (50 ml), c. sulfuric acid (5 drops) was added, the mixture was heated for 2 h and worked up in the normal manner. With EC 5146B a viscous red oil (16.0 g) was obtained which afforded an ether soluble oil (14.3 g, used for analytical studies) and a purple-red ether insoluble semi-solid (0.65 g). Thin layer chromatography (Kieselgel, acetone) of the insoluble material gave three bands which each showed intense infrared signals at ν_{max} 3400 and 1740 cm^{-1} together with a significant peak at 1610 cm^{-1} . The crude material had δ (CD_3SOCD_3): 6.3-8.0 (broad, poorly structured), 5.16 (broad, weak), 3.83 (broad) and only minor aliphatic peaks. Relative integral ratios were 4.6:1:11. Examination of the material by gas chromatography gave no new peaks, possibly because the main components were insufficiently volatile. The ether soluble oil (14.3 g) showed an additional peak by gc analysis which gave m/e : 271 (5%), 217 (10), 200 (13), 199 (100), 185 (27), 166 (11), 139 (32), 138 (11), 125 (15), 121 (16), 97 (25), 96 (24), 87 (24), 86 (18), 84 (17), 83 (15), 81 (13), 74 (30), 69 (53), 67 (12), 59 (13), 57 (25), 56 (63), 55 (65), 45 (32), 43 (28), 41 (68). This material is considered to be the methyl ester of neopentyl sebacate.

3.6 Molecular and Equivalent Weight Determinations

Number average molecular weights were obtained by VPO using acetone as solvent at 37.5° and methyl stearate as a calibration standard. Acid equivalent weights were determined by pmr spectroscopy as described earlier and relevant spectral data is listed under Materials, section (b). Acid equivalent weights were also obtained by titration of samples in acetone or dimethylformamide using 0.1N ethanolic sodium hydroxide and either phenolphthalein as indicator or a potentiometric titration apparatus equipped with calomel and glass electrodes.

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T A B L E 1

COMPOSITION OF POLYESTER PREPOLYMERS^a

ALCOHOLS	EC 5106B		EC 5146B
	I	II	I
	48.8%	37.4%	49%
Unassigned glycol	trace	2.0	1.6
Neopentyl glycol	46.3	32.4	43.9
Diethylene glycol	1.0	1.3	trace
Trimethylolethane	-	-	0.4
Trimethylolpropane	1.5	1.7	3.1
ACIDS	51.2%	62.6%	51%
Sebacic acid	39.7	52.3	46.6
2-Methyloctanedioic acid	8.3	6.6	1.5
Undecanedioic acid	1.9	2.1	1.6
Deodecanedioic acid	1.3	1.6	1.4

^a Data based on gc results using following molar responses:

trimethylolpropane triacetate	1.0
dimethyl sebacate	0.73
neopentyl glycol diacetate	0.45

I: Based on reaction with LiOMe, Ac₂O

II: Based on reaction with LiOMe, MeOH-H⁺, Ac₂O

T A B L E 2

MOLECULAR WEIGHT AND ACID EQUIVALENT WEIGHT DETERMINATIONS

MATERIAL	METHOD		
	VPO ^a	POTENTIOMETRIC TITRATION ^b	PMR ^b
EC 5106B	1300	1050 (1880) ^c	950
Hydrolysed EC 5106B	720	670 (685) ^c	580
Degraded EC 5106 Sealant	1020	1070 (940) ^c	-
Degraded EC 5146 Sealant	-	475	-

a Number average molecular weight

b Acid equivalent weight

c From reference 10

T A B L E 3

X-RAY FLUORESCENCE ANALYSIS OF FILLERS

ELEMENT	SEALANT			
	EC 5106		EC 5146	
	Counts/Sec	Wt%	Counts/Sec	Wt%
Ti	96500	74	86000	51
Si	2310	22	6500	43.5
Zn	2370	1	3140	1.5
Al	360	3	480	4
Ca	850	trace	1920	trace

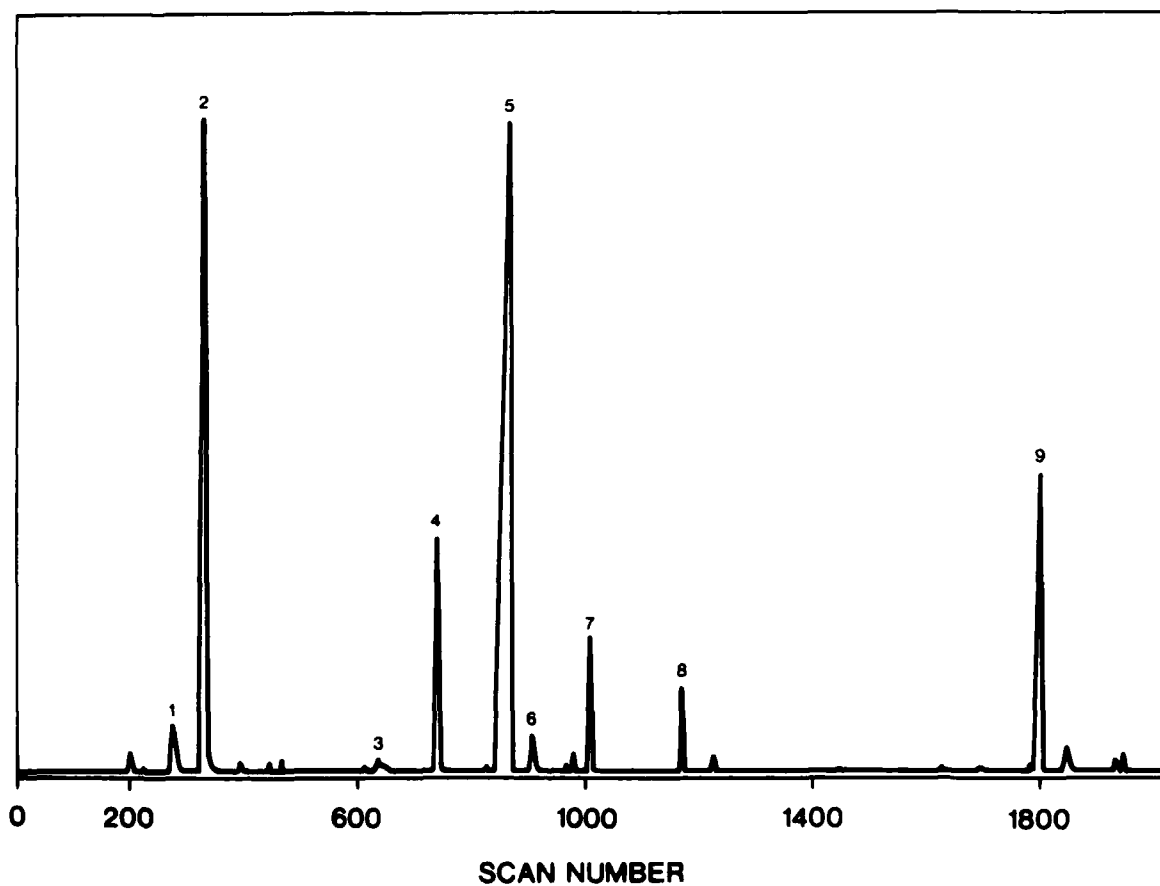


FIGURE 1

GC spectrum of degraded and acetylated EC 5146B. Peak assignments: 1, unidentified glycol acetate; 2, neopentyl glycol diacetate; 3, trimethylolethane triacetate; 4, trimethylolpropane triacetate; 5, dimethyl sebacate; 6, suspected dimethyl 2-methyloctanedioate; 7, dimethyl undecanedioate; 8, dimethyl dodecanedioate; 9, sebacate ester (5).

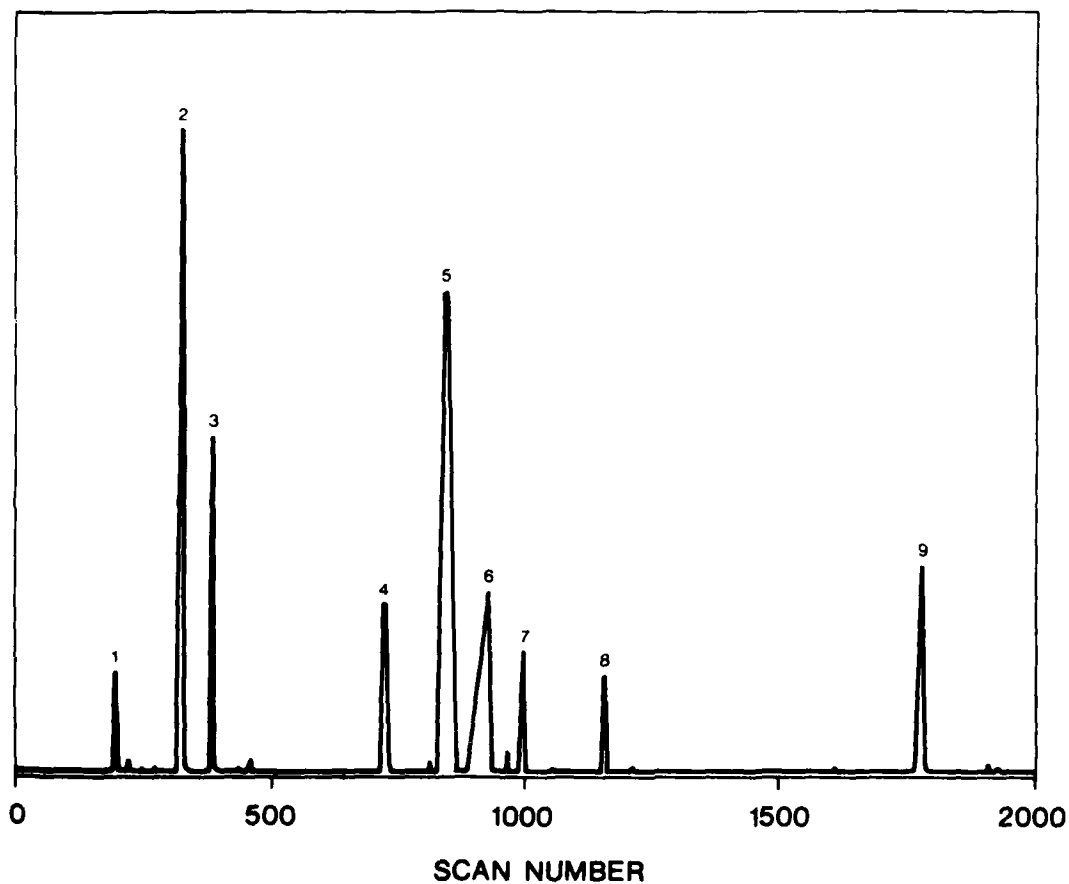


FIGURE 2

GC spectrum of degraded and acetylated EC 5106B. Peak assignments: 1, dichloromethane; 2, neopentyl glycol diacetate; 3, diethylene glycol diacetate; 4, trimethylolpropane triacetate; 5, dimethyl sebacate; 6, suspected dimethyl 2-methyloctanedioate; 7, dimethyl undecanedioate; 8, dimethyl dodecanedioate; 9, sebacate ester (5).

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