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**UNITED STATES AIR FORCE  
ARMSTRONG LABORATORY**

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**ATMOSPHERIC CHEMISTRY OF  
COATING SYSTEMS**

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14. Abstract Understanding the atmospheric impact of Air Force operations is important for maintaining environmental compliance. A detailed description of emissions is important for derivation of operational atmospheric impact. The atmospheric assessment of current and future Air Force coating systems was conducted by identifying and quantifying the volatile organic compounds (VOC) emitted by the coating system. This information was then fed into an incremental reactivity calculation to determine the VOC's ozone forming potential. The summation of the VOC incremental reactivity times VOC concentration is used to determine an incremental reactivity for the coating. The coatings that contained m-xylene, o-xylene, ethyl benzene, and nitroethane had the largest incremental reactivities. The hydroxyl radical rate constant and proposed atmospheric reaction mechanism of ethyl 3-ethoxypropionate was also determined.					
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## **PREFACE**

This report was prepared by Armstrong Laboratory's Environics Directorate, 139 Barnes Drive, Suite 2, Tyndall AFB, FL 32403-5323, as part of the requirements of F-08635-93-C and under a work agreement with the Wright Laboratory's Materials Directorate.

## EXECUTIVE SUMMARY

### A. OBJECTIVE

The objective of this research effort was to determine the atmospheric impact of current and future Air Force coatings systems by speciating and quantifying the coating's volatile organic compound (VOC) emissions and using that information to calculate the coating's incremental reactivity, or ozone (O<sub>3</sub>)-producing potential.

### B. BACKGROUND

The Air Force must comply with Clean Air Act Amendments and preceding legislation. Therefore, a detailed understanding of the atmospheric impact of Air Force operations is vital in preventing costly fines and in preventing further pollution of the atmosphere. Coatings used by the Air Force are significant sources of uncharacterized volatile organic compounds (VOC) emissions. VOCs have been shown to be involved in the production of tropospheric ozone (O<sub>3</sub>), a regulated pollutant. VOCs could also be toxic. Since the detailed atmospheric chemistry of several of these chemicals has never been investigated, experimental atmospheric research coupled with incremental reactivity calculations is useful to more accurately assess the atmospheric impact of coatings emissions. The information generated by this research will be used to help the Air Force select the most "atmospherically benign" coating system.

### C. SCOPE

The following coating systems were studied:

<u>COATING</u>	<u>MANUFACTURER</u>
MIL-P-23377F TYPE I CLASS I	PRATT & LAMBERT
TT-P-2760A	DEFT
MIL-C-85285B	DEFT
MIL-C-83286B	DEFT
TT-P-2756	DEFT
724-500/724-501	PRATT & LAMBERT
785 SERIES	PRATT & LAMBERT
44-GN-36	DEFT
755 SERIES	PRATT & LAMBERT
513X423B	COURTLAUDS
MIL-C-85285	COURTLAUDS
EEAE145A/B	SPRAYLAT
EUBG167A/B	SPRAYLAT
EEAE136A/B	SPRAYLAT
44W16	DEFT
55GY02	DEFT
MIL-P-23377G TYPE II CLASS C	DEFT
K9800-K43	US PAINT
K8032	US PAINT
K1067-K45	US PAINT

During the study, samples of the coating systems were analyzed to speciate and quantify their VOC emissions. The following tasks were completed:

1. Construction of a sampling system to collect vapors from the coating system.
2. Development of analytical method for collecting and analyzing the collected coating vapors.
3. Incorporation of VOC incremental reactivity calculations with coating emission data to determine the coating's ozone-forming potential.

#### D. METHODOLOGY

The atmospheric impact of the coating systems was determined, using individual VOC incremental reactivity calculations, coupled with a detailed description of coating system emissions. This resulted in computing the amount of ozone (O<sub>3</sub>) generated by each coating system. The concentrations and identification of VOCs in the coating emissions were determined by combining gas chromatography, mass spectroscopy and fourier transform infrared spectroscopy (GC/MS/FTIR) techniques.

#### E. TEST DESCRIPTION

The coating systems were investigated under simulated tropospheric conditions. Each coating system was mixed according to label instructions, and the coating emissions were collected by cryogenically trapping the head space above the coating. VOCs were identified and quantified by GC/MS/FTIR. The results of the VOC analysis were used to calculate the ozone-forming potential, incremental reactivity, of each coating system. Because no information on the atmospheric behavior of ethyl 3-ethoxypropionate existed, it was investigated in detail. The OH rate constant for ethyl 3-ethoxypropionate was determined using the relative rate technique. The products of the OH + ethyl 3-ethoxypropionate reaction were determined and an atmospheric reaction mechanism for ethyl 3-ethoxypropionate was proposed. These new research results were used to determine an incremental reactivity value for ethyl 3-ethoxypropionate.

#### F. RESULTS

The following summarizes the results for the laboratory investigations:

1. The coating systems contain a more complex mixture of organics and oxygenated organics than reported on the Material Safety Data Sheet (MSDS).
2. Coatings that contain aromatic compounds such as *m*- and *o*- xylene, ethyl benzene, and methyl benzene (toluene) have large incremental reactivity.

3. The rate constant for OH + ethyl-3-ethoxypropionate from this research was  $22.86 \pm 1.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  yielding a tropospheric lifetime (1/e) of approximately 12 hours.

4. The atmospheric reaction mechanism of ethyl-3-ethoxypropionate is complex; reaction products consist of several unusual oxygenated organic compounds.

5. The following table displays the Maximum Incremental Reactivity (MIR) of each coating system studied. The wide range of  $\text{MIR}_{\text{Coating}}$  values is evidence of the variability of atmospheric impact from one coating system to another. The units of the summation of concentration  $\text{VOC}_{\text{observed}}$  times the  $\text{MIR}_{\text{VOC}}$  yield a result in grams of ozone formed per liter of coating system.

<b>PAINT NAME</b>	<b><math>\text{MIR}_{\text{Coating}}</math> <math>\Sigma(\text{MIR} \cdot \text{VOC})</math> (g O<sub>3</sub>/l of paint)</b>
MIL-P-23377F t1c1	38.22
TT-P-2760A	9.00
MIL-C-85285B	5.62
MIL-C-83286B	3.81
TT-P-2756	1.60
S 3 P&L724-500/01	5.05
S3 P&L 785's	21.38
S4 D 44GN36	32.16
S4 P&L 755's	2.92
S6 C513X423B	11.65
S6C MIL-C-85285	7.11
S14SEEA145A/B	3.28
S14,15 SEUBG167A/B	2.35
S15 SEEA136A/B	14.33
S20 D44W16	36.09
S20 D55GY02	0
MIL-P-23377G TII CC D02GN070	2.27
S23 US K9800-K43	24.04
S23 US K8032	24.04
US K1067-K45	2.23

## G. CONCLUSIONS

Coating systems emit a wide variety of volatile organic compounds. Aromatics (benzenes and xylenes), ketones, cyclic ketones, alcohols and nitro-organic species were observed in the emissions of the above coating systems. While the incremental reactivity calculations used here are currently the best of their kind, there are still several significant gaps in the detailed knowledge of the atmospheric chemistries of VOC. In the calculation these gaps are filled by educated assumptions and further research is needed to verify

these assumptions. A small change in the mechanism can lead to a major change in the calculated incremental reactivity.

The OH rate constant and atmospheric reaction mechanism of ethyl-3-ethoxypropionate have never been determined before this report. This oxygenated organic has a tropospheric lifetime ( $1/e$ ) of approximately 12 hours and the OH + ethyl-3-ethoxypropionate reaction products consist of unusual new oxygenated organic compounds. The proposed atmospheric transformation mechanism and the measured OH rate constant were used to determine the incremental reactivity of ethyl-3-ethoxypropionate.

## H. RECOMMENDATIONS

Using the table from the results of this research, selection of the coating with the lowest  $MIR_{Coating}$  ( $\Sigma(MIR*VOC)$ ) value should yield a minimal atmospheric impact. For two-part coating systems the lowest combined  $\Sigma(MIR*VOC)$  value should yield a minimal atmospheric impact. VOC MIR calculations will greatly improve by understanding the details of VOC atmospheric chemistry. The replacement of chemicals such as methyl ethyl ketone, 4-methyl-2-pentanone (methyl isobutyl ketone), ethyl benzene, methyl benzene, and xylene(s) would lower the  $MIR_{Coating}$  and reduce the release of Hazardous Air Pollutants (HAPs). From the data collected, coating systems 4, 20 and 23 produce the largest ozone concentration contain toxic HAPs, and are therefore not recommended for use by the Air Force. Systems 6 and 15 are also not recommended because they emit triple the toxic HAPs of the remaining systems. Therefore the recommended systems ranked in order of environmental acceptability are 17, 14, and 3 (system 3 has significant ozone potential, but low HAPs).

Determining the OH kinetics, OH + VOC reaction products, and developing more realistic VOC atmospheric reaction mechanisms are areas that continue to need research emphasis. The fruits of this research will benefit the Air Force in at least two ways:

1. Provide avenues of chemical design to build a good solvent with "atmospherically benign" properties.
2. Develop methods to maintain compliance and prevent costly (time and money) fines by intelligent emission practices.

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## SECTION I

### INTRODUCTION

#### A. OBJECTIVE

The objective of this research project is to determine the atmospheric photochemical reactivity of selected coating systems in present or future use by the US Air Force. This information will be used to assess the environmental impact of coatings emissions. Vapor recovery and scrubbing devices are costly. The type of scientific information gained from this study will provide a basis for cost-effective environmental control strategies consistent with federal, state, and local regulations dealing with air quality controls.

The volatile organic compound (VOC) concentrations and identifications were determined from analysis of coating emissions. This information was coupled with each VOC's incremental reactivity value, tendency to produce ozone ( $O_3$ ), yielding a basis for assessing each coating system. Ozone is a regulated pollutant, and while not directly emitted, is formed in the atmosphere as a product of VOC atmospheric oxidation [1]. The Environmental Protection Agency is revising its tropospheric ozone concentration regulation which will most likely increase the number of facilities out of compliance. The research results presented here will aid in the selection of coating system(s) to prevent significant  $O_3$  formation.

## B. BACKGROUND

Twenty years ago, the first currently accepted chemical mechanisms to explain the formation of photochemical smog were presented. However, even before these were published, it was recognized that the formation of ozone in urban environments resulted through a series of branching chain reactions involving hydrocarbons (HCs) and oxides of nitrogen ( $\text{NO}_x$ ). What was not recognized was the crucial role played by the hydroxyl radical (OH) to initiate the photochemical chain. Chain carriers in these mechanisms also included organic peroxide and alkoxy radicals and the hydroperoxyl radical ( $\text{HO}_2$ ). These branching chain reactions serve to regenerate OH, and in the process many organic products are formed, including aldehydes and ketones, peroxyacyl nitrates, organic nitrates and peroxides, and other products. During photooxidation nitric oxide (NO) is converted to nitrogen dioxide ( $\text{NO}_2$ ) which then photolyses to produce ozone ( $\text{O}_3$ ).

In urban environments, oxides of nitrogen (particularly NO) required for these reactions to occur come from combustion primarily from automobile exhaust and power plants. On the other hand, sources of hydrocarbons which contribute to the atmospheric load are varied and numerous. They include automobile emissions, industrial emissions, other fossil fuel combustion, commercial emissions, household use of cleaning agents and solvents, natural emissions, and other sources. Evaluating the contribution of each of these sources to the total hydrocarbon loading in a particular regional area is difficult and is being addressed by the U.S. Environmental Protection Agency. Since much of the volatile organic emissions loading can come from numerous small sources, it has become

imperative for local and state governments to regulate many generators of volatile organic emissions.

The US Air Force in the course of its normal, peacetime operations performs many regular activities which result in emission of volatile organic compounds (VOCs). A common maintenance operation is the stripping and repainting of aircraft. This process requires large quantities of organic solvents that evaporate into the atmosphere. The Department of Defense (DoD) has committed itself to complying with local and state regulation, therefore, the impact of these evaporated solvents must be evaluated. In addition, there is a need for understanding the fundamental effects a VOC has on a local region as well as globally. These effects can be considered by the following series of questions: (1) What is the atmospheric lifetime of the emitted VOC; (2) What are the identities and yields of the products formed during the atmospheric degradation of the VOC; and (3) Is the VOC effective in producing ozone when oxidized in the presence of  $\text{NO}_x$  (4) Are the VOC and/or its products toxic? The answer to these questions is ultimately grounded in understanding the gas-phase kinetics and mechanisms of these compounds when photooxidized under atmospheric conditions.

The VOCs from these solvents interact with trace chemical species such as OH and  $\text{NO}_3$  in the atmosphere. These reactions generate products that can further react generating a host of other chemical species. This series of reactions has been shown to eventually produce ozone and a variety of oxygenated and nitrogenated organic species [1]. Therefore research on the solvents and their interaction with the atmosphere is very useful to determine the environmental impact of a maintenance operation. For the program described

in this report, selected VOCs were studied to determine their OH rate constants and the products of the atmospheric reactions.

### C. SCOPE/APPROACH

Assessing the atmospheric impact of a coating system requires a detailed knowledge of the coating's VOC emissions. The concentration and type (i.e. alcohol, aromatic, ketone, etc.) of VOC emitted can be used to calculate the Maximum Incremental Reactivity (MIR) of a coating system.  $MIR_{VOC}$  is a calculation of the amount of  $O_3$  formed per gram of individual VOC. The larger the  $MIR_{Coating}$  for the coating system, the more tropospheric  $O_3$  produced, resulting in potential noncompliance.

Each coating system was evaluated by collecting the emissions from a sample of the system and identifying and quantifying the VOCs observed. The collected coating emissions were analyzed by gas chromatography/mass spectroscopy/infrared spectroscopy (GC/MS/FTIR) yielding VOC identification and concentration. The coupling of mass and infrared spectroscopies minimized incorrectly identified VOCs. A  $MIR_{VOC}$  was determined for each VOC. Where no previous  $MIR_{VOC}$  existed for a VOC both the OH rate constant and the reaction mechanism had to be determined.

As discussed in the background section, there are three general areas for study to evaluate the fate of emitted VOCs: (1) The reaction rate of VOC + OH, ozone ( $O_3$ ), and  $NO_3$ , and photolysis; (2) Identification of the mechanistic pathways and product yields; and (3) The overall potential for the VOC to form ozone under atmospheric conditions. Numerous studies have examined each of these aspects from a wide array of VOCs, although not all aspects have been considered for each compound studied.

In general, kinetic studies are concerned only with the rate of removal of chemical species. Mechanistic studies, on the other hand, are concerned with the identity and yield of products generated during the photochemical degradation. However, once the kinetic studies have been completed (as is often the case) a single process is responsible for a large fraction of the total atmospheric removal. Thus, mechanistic studies are frequently focused on the reactions of a single radical (or photolysis). Removal by the hydroxyl (OH) radical is the predominant path for atmospheric removal of many VOCs, thus most mechanistic studies focus on products generated from reaction by OH.

A number of methods have been used over the years to obtain product information from elementary chemical reactions. These have included both spectroscopic and chromatographic methods. For the coating VOC mechanisms, a combination GC/MS/FTIR system has been implemented.

Most of the volatile chemicals in the coating systems have received very little attention from the atmospheric research community. This research project will fill in these knowledge gaps and add significant new insights into the atmospheric impact of the VOC in coating systems with the ultimate goal to quantify point (3) above.

Table 1 lists the painting systems to be evaluated by AL/EQL. The final product of this research is the atmospheric assessment of each coating system.

Table 1.

COATING SYSTEMS MATRIX  
FOR  
ATMOSPHERIC CHEMISTRY ASSESSMENT

Mil Spec Coating Systems Currently Used

<u>Primers</u>	<u>Topcoats</u>	<u>Self-Priming Topcoat</u>
MIL-P-23377F, Type I, Class 1	MIL-C-85285B	TT-P-2756
MIL-P-23377F, Type I, Class 2	MIL-C-83286B	
MIL-P-23377F, Type II, Class 2		
MIL-P-85582B, Type II, Class 1B		
TT-P-2760, Type I, Class 1		
TT-P-2760, Type I, Class 2		

Coating Systems from High Performance Aerospace Coating System Program

<u>System No.</u>	<u>Primer Product I.D.</u>	<u>Supplier</u>	<u>Topcoat Product I.D.</u>	<u>Supplier</u>
3	724-500/724-501	Pratt & Lambert	785-637/785-000/785-11B	Pratt & Lambert
4	MIL-P-85582B, Type II, Class 1B	Deft	755-637/756-201	Pratt & Lambert
6	513X423B	Courtaulds	MIL-C-85285	Courtaulds
7	513X423B	Courtaulds	RW 3189-83	Courtaulds
14	EEAE145 A/B	Spraylat	EUBG167 A/B	Spraylat
15	EEAE136 A/B	Spraylat	EUBG167 A/B	Spraylat
17	-	-	TT-P-2756	Deft
20	44-W-16	Deft	55-GY-002	Deft
23	S9800-K13	U.S. Paint	K-8032	U.S. Paint
			Awlgrip	U.S. Paint

## SECTION II

### EXPERIMENTAL

#### A. COATING VOC SAMPLING

The sampling method used during the course of these investigations closely simulates an actual condition of paint application. Each component of the coating system as well as the mixed complete system was placed in a small vial. A 1/8th-inch Teflon<sup>®</sup> regulated sampling line was run from the open top of the vial to the cryogenic sample loop [2]. A small vacuum pump/electronic flow controller system maintained a 25 mL/min regulated flow through the line, and typically, a 75 mL sample was collected. The sample loop (1.3 ml silanized, glass-bead filled trap) was maintained at -100°C and flash heated to 264°C for injection onto the gas chromatograph via a heated rotary valve. Compound separation was achieved using a Restek Rt<sub>x</sub> 502.2-column (0.53 mm ID, 30-meter 3.0 μ film thickness) with an Hewlett-Packard (HP) 5890 II Plus GC equipped with an HP 5965 B Infrared detector (IRD) and an HP 5971 mass selective detector (MSD). Helium (UHP, Air Products) was used as the carrier gas and the GC oven temperature was ramped from 35 to 220°C during a typical experiment. The column effluent is split between the HP 5971 and HP 5965 B using a glass capillary "Y" splitter (Restek Corp. and Supelco). This affords the simultaneous mass spectrum detection and infrared spectrum collection of analyte peaks. The IRD collects an IR spectrum every 0.67 seconds ( 8 cm<sup>-1</sup> resolution with each four scans (1.5 scans/second) averaged). The MSD collects data in the scan mode at 1.9 scans/second.

The system schematic is shown in Figure 1.

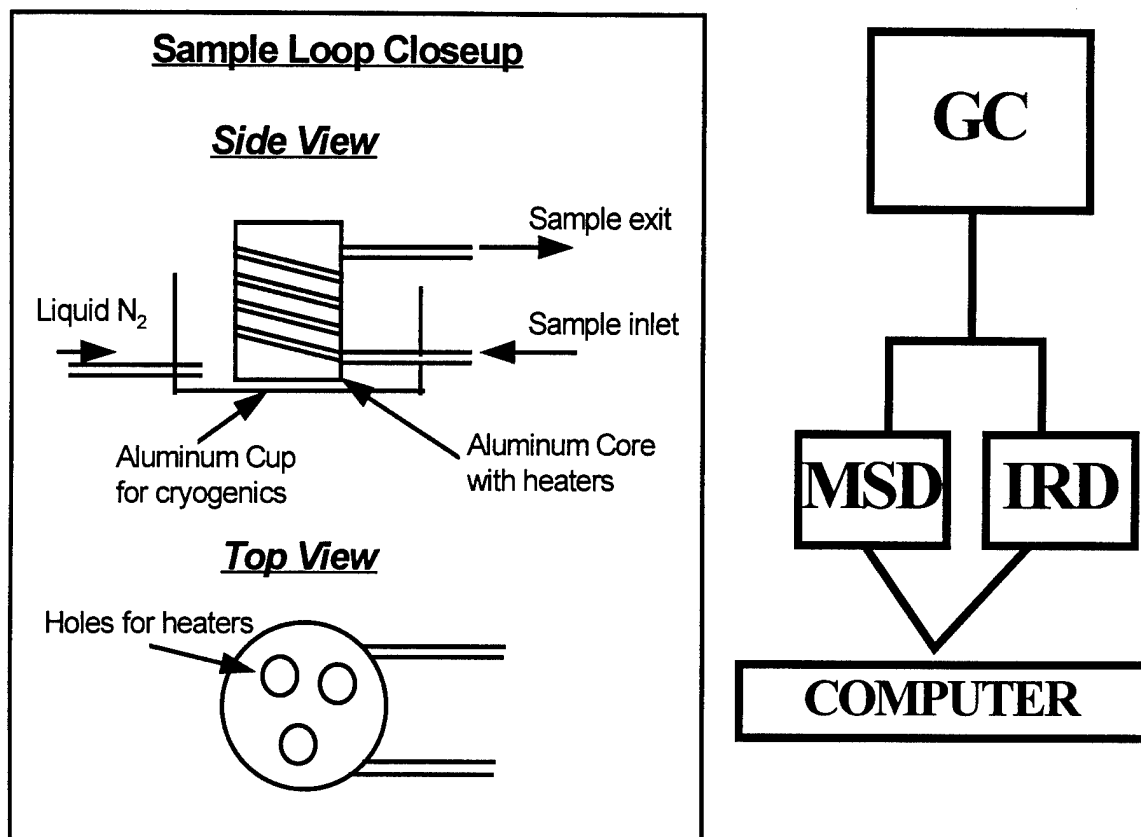
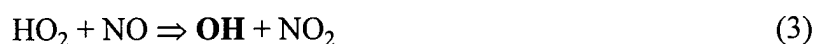
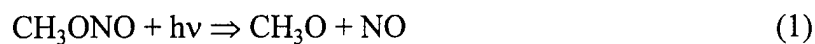


Figure1. The coatings collection apparatus and detail of sample loop. Abbreviations are explained in the text.

## B. HYDROXYL RADICAL GENERATION

Hydroxyl radical are generated in Teflon<sup>®</sup>-film bags by the photolysis of methyl nitrite in air [3]:



Methyl nitrite was synthesized by dropwise addition of 50% sulfuric acid into a methanol-saturated solution of sodium nitrite according to the procedure of Taylor *et al.* [4]. The methyl nitrite purity was confirmed by GC/FTIR/MS, collected in a lecture bottle and stored at room temperature.

For the OH kinetic experiments, irradiations are carried out in 30- to 100- liter, 2-mil FEP Teflon<sup>®</sup> surrounded by black (UV) and actinic lights. The bag and lamps are housed inside a wooden box lined with reflective foil.

## C. RELATIVE RATE TECHNIQUE

The relative rate technique is used to measure OH rate constants for the paint VOC, ethyl 3-ethoxypropionate (EEP) [3]. The experiment consists of placing the compound of interest (the sample S), a reference compound (R), and OH source, and an excess of NO into a Teflon<sup>®</sup> bag. This mixture is then irradiated for specific time intervals. After each irradiation a portion of the contents (50-300 mL) from the Teflon<sup>®</sup> chamber is collected onto a cryogenically cooled sample loop, flash heated, and injected

onto a gas chromatograph. The concentrations of the reference and the sample compound are used to determine the OH rate constant for the sample compound.

The OH generated by the photolysis of methyl nitrite ( $\text{CH}_3\text{ONO}$ ) react with the reference, R, and the sample, S,:



Assuming the reaction with OH is the only significant loss process for both the reference and the sample, the rate equations for reactions (4) and (5) are combined and integrated resulting in the following equation:

$$\ln \frac{[\text{S}]_0}{[\text{S}]_t} = \frac{k_S}{k_R} \ln \frac{[\text{R}]_0}{[\text{R}]_t} \quad (6)$$

Where  $[\text{X}]_0$  refers to the species concentration before OH generation and  $[\text{X}]_t$  is the species concentration at some arbitrary reaction time,  $t$ . Plots of  $\ln([\text{S}]_0/[\text{S}]_t)$  versus  $\ln([\text{R}]_0/[\text{R}]_t)$  are linear (see Figures 2 and 3) with a slope of  $k_S/k_R$  and an intercept of zero. Therefore multiplying the slope of the linear least squares fit of the data by the established rate constant,  $k_R$ , yields  $k_S$ .

$$k_S = k_R \times \text{slope} \quad (7)$$

## D. VOC EXPERIMENTAL PARAMETERS

### 1. OH Rate Constant Experiments

A reference compound (1 to 3 ppmv), EEP (1 to 3 ppmv), methyl nitrite (5 to 10 ppmv as the OH source), nitric oxide (NO) (1 to 2.5 ppmv added to support the OH

formation and suppress ozone ( $O_3$ ) reactions) were mixed for approximately 45 minutes and photolysis reactant concentrations ( $[S]_0$  and  $[R]_0$ ) are measured. Approximately 50 to 200 milliliters of the chamber contents are sampled by vacuum collection onto a glass-bead-filled sample loop ( approximate volume 1.3 mL) cryogenically cooled to a specified temperature, typically  $-100^\circ\text{C}$ , then flash-heated and injected onto a megabore or capillary gas chromatographic column [2]. The reactant concentrations are measured by gas chromatography (Hewlett-Packard Model 5890 GC) with flame ionization detection (FID). Maximum irradiation times for EEP rate constant runs are 80 s with an initial 5 to 7 s followed by others at 3 to 5 s increments. The total irradiation time was kept as short as possible to prevent complications for the reaction products. Each experiment consists of 5 irradiations with the total loss of the sample and reference compounds under 50%. For EEP, a Restek Stabilwax<sup>®</sup>, 30-m, 0.53mm ID column is used. The column choice changes are based on the polarity of the compound of interest, resolution of reference and sample, and resolution of reaction products. Typically, the GC oven temperature is programmed from 35 to  $210^\circ\text{C}$  with helium as the carrier gas.

The key assumption of the relative rate technique is the decrease of both the reference and the sample is due solely to reaction with photolytically generated OH. Typical experimental mixtures of methyl nitrite, sample and reference are left in the dark for average experimental period (up to 8 hours). For EEP there was no observable loss. EEP was also exposed to chamber lights to check for photolysis; again, no loss was observed.

Separate experiments in which mixtures of methyl nitrite, NO and sample *or* reference are irradiated demonstrate that primary and secondary reaction products do not overlap with the sample or reference gas chromatograph retention times.

## 2. Product determination

### a. Gas chromatography/mass spectrometry/ infrared spectroscopy

Identifying and quantifying the products formed in the OH + VOC reaction are necessary to better understand atmospheric reaction mechanisms. Product identification is also necessary to evaluate the environmental impact of a VOC. The reaction products could be more harmful than the compound of interest.

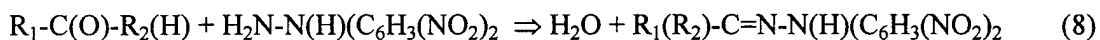
Product identifications are performed using both the small (30 - 100 L) and large (3,000 L) chambers coupled to a Hewlett-Packard (HP) 5890 II Plus GC equipped with an HP 5965 B Infrared detector (IRD) and an HP 5971 mass selective detector (MSD). The column effluent is split between the HP 5971 and HP 5965 B using a glass capillary "Y" splitter (Restek Corp. and Supelco). This affords the simultaneous mass spectrum detection and infrared spectrum collection of analyte peaks. The IRD collects an IR spectrum every 0.67 seconds (  $8\text{ cm}^{-1}$  resolution with each four scans (1.5 scans/second) averaged). The MSD collects data in the scan mode at 1.9 scans/second.

The chamber is filled with air, NO (2 to 5 ppmv), methyl nitrite (2 to 5 ppmv) and the VOC of interest (2 to 20 ppmv). The contents are irradiated initiating reactions (1)-(3). The OH reacts with the VOC and products are formed. The chamber contents were analyzed before irradiation to collect a background and analyzed after each subsequent irradiation to monitor VOC loss and product growth.

Approximately 50 to 200 mL of the small *or* large chamber contents are sampled by vacuum collection onto a glass bead filled sample loop (approximate volume 1.3 mL) cryogenically cooled to a specified temperature, typically -100°C, then flash-heated and injected onto a megabore or capillary gas chromatographic column. Helium is used as the carrier gas and the GC oven temperature was ramped from 35 to 220°C.

b. Aldehydes and Ketones

Aldehydes and ketones have similar infrared signatures and are therefore difficult to quantify by FTIR, and they can be difficult to analyze by gas chromatography. An analytical method by which these aldehyde and ketone reaction products are derivitized to hydrozones and analyzed by high pressure liquid chromatography (HPLC) has been a successful technique [5].



An HP 1050 HPLC is used with a single DuPont Zorbax™ ODS column (25 cm x 46 cm, 5 µm particle size). Methanol and acetonitrile, both HPLC grade, were obtained from Fisher Scientific and used as received. Water was deionized (18 megaohm) using a Milli-Q® system. A 26-minute ternary gradient mobile phase at a constant flow of 1ml/min is used as follows:

*Water*- 40% decreased linearly to 25% at 10 minutes, further decreased to 15% at 20 minutes and held constant to 26 minutes.

*Acetonitrile*- 20% decreased linearly to 5% at 10 minutes and held constant to 26 minutes.

*Methanol*-40% increased linearly to 70% at 10 minutes, further increasing linearly to 80% at 20 minutes, and held constant to 26 minutes.

c. Quantification

Quantification data are used to account for the loss of the sample due to OH/VOC reaction. This information is used to more clearly describe the reaction mechanism.

After the products are identified, experiments to measure the loss of VOC and the generation of products are done.

E. INCREMENTAL REACTIVITY

The regulatory agencies are desperate to have a simple, predictable method for determining the ozone forming potential of a given compound released into a polluted atmosphere. This need is hampered by the lack of detailed atmospheric kinetic and mechanistic information for VOC, the lack of detailed knowledge of the pertinent reactive processes and reactive species concentrations, and by the fact that not all VOCs produce the same amount of ozone. Also, the type and concentrations of pollutants ( i.e. oxides of nitrogen ( $\text{NO}_x$ ) and other VOCs) that drive the formation of  $\text{O}_3$  are different at different times of the day and at different locations. One of the most significant factors for  $\text{O}_3$  formation is the  $[\text{VOC}]/[\text{NO}_x]$  ratio [1,6], but in the complex system of the atmosphere there is not a simple relationship correlating the ratio to  $\text{O}_3$  concentration. Distillation of all of these atmospheric effects and processes into a simple to understand, single number is a daunting task. But, because this is such an important issue and a best educated guess is better than nothing at all, the California Air Resources Board (CARB) has adopted a model developed by Bill Carter [7] to calculate the incremental reactivity

of a VOC. The model calculates, for 119 different base case scenarios, the average amount of O<sub>3</sub> formed when a small amount of a VOC is emitted. This average is a single number called the incremental reactivity. These calculations put each VOC on more equal footing, since not all VOC have the same ozone production potential.

The Maximum Incremental Reactivity (MIR<sub>VOC</sub>) was used as the incremental reactivity metric and is derived by adjusting (mathematically) the NO<sub>x</sub> emissions, and hence the [VOC]/[NO<sub>x</sub>] ratio, in each base case to yield the highest incremental reactivity. MIR<sub>VOC</sub> calculations were used to derive the ozone forming potential of each coating system (MIR<sub>Coating</sub>) investigated.

The incremental reactivity for each coating system was determined by multiplying the calculated incremental reactivity of each observed component by the observed concentration of that component and summing over all observed components in the coating system.

$$\text{Coating Incremental Reactivity} = \sum_{i=1 \text{ to } n} [\text{component}]_i * \text{Maximum Incremental Reactivity of } i \quad (9)$$

The VOC concentration was calculated in units of grams VOC/L of paint and the Maximum Incremental Reactivity (MIR<sub>VOC</sub>) was calculated in units of grams of O<sub>3</sub> formed/grams VOC. The multiplication and summation of MIR<sub>VOC</sub> for each coating yielded results (MIR<sub>Coating</sub>) with units of grams of O<sub>3</sub>/L of paint.

## SECTION III

### RESULTS

#### A. COATINGS VOC SPECIATION AND CONCENTRATIONS

Using the method described above in Section II, each paint listed here was analyzed. What is reported for each paint is the *complete* system. Each component of each paint system was investigated, but in no case did another VOC arise from chemistry of combining paint components. No compound was observed in the complete system that was not observed in the individual components. What follows is a list of each paint investigated up to this time, the volatile components, and an approximate concentrations of the VOCs in the vapor above the paint sample. The values are in units of grams/L of paint.

##### *MIL-P-23377F Type I Class I*

Methyl ethyl ketone (MEK,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ) [0.197], 4-methyl-2-pentanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_3$ ) [2.73], isobutyl acetate ( $(\text{CH}_3)_2\text{CHCH}_2\text{OC}(=\text{O})\text{CH}_3$ ) [2.72], methyl benzene ( $\text{CH}_3\text{C}_6\text{H}_5$ ) [2.82], ethyl benzene ( $\text{CH}_3\text{CH}_2\text{C}_6\text{H}_5$ ) [0.55], 1,3-dimethyl benzene ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ ) [2.19], 1,4-dimethyl benzene ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ ) [2.82]

##### *TT-P-2760A*

Methyl ethyl ketone (MEK,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ) [5.63], 4-methyl-2-pentanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_3$ ) [1.96], butyl acetate ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(=\text{O})\text{CH}_3$ ) [0.5], ethyl-3-ethoxypropionate ( $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-C(O)-O-CH}_2\text{CH}_3$ , EEP) [0.17]

##### *MIL-C-85285B*

4-methyl-2-pentanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_3$ ) [0.39], butyl acetate ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(=\text{O})\text{CH}_3$ ) [0.05], cyclohexanone ( $\text{C}(=\text{O})\text{C}_5\text{H}_{10}(\text{cyclo})$ ) [0.19], ethyl-3-ethoxypropionate ( $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-C(O)-O-CH}_2\text{CH}_3$ , EEP) [ 0.17]

**MIL-C-83286B**

Methyl ethyl ketone (MEK,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ) [4.216], ethyl acetate ( $\text{CH}_3\text{CH}_2\text{OC}(=\text{O})\text{CH}_3$ ) [1.38], 4-methyl-2-pentanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_3$ ) [0.196], butyl acetate ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(=\text{O})\text{CH}_3$ ) [0.091], methyl benzene ( $\text{CH}_3\text{C}_6\text{H}_5$ ) [0.08], ethyl benzene ( $\text{CH}_3\text{CH}_2\text{C}_6\text{H}_5$ ) [0.08], 1,3-dimethyl benzene ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ ) [0.054], ethyl-3-ethoxypropionate ( $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-C(O)-O-CH}_2\text{CH}_3$ , EEP) [1.14]

**TT-P-2756**

Butyl acetate ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(=\text{O})\text{CH}_3$ ) [1.36], 2-heptanone ( $\text{CH}_3\text{C}(=\text{O})(\text{CH}_2)_4\text{CH}_3$ ) [0.31], ethyl-3-ethoxypropionate ( $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-C(O)-O-CH}_2\text{CH}_3$ , EEP) [0.23]

**System 3 Primer (Pratt and Lambert 724-500/724-501)**

2-pentanone ( $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$ )[1.33], 4-methyl-2-pentanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_3$ ) [0.47], 5-methyl-2-hexanone ( $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{CH}_3$ ) [0.5], ethyl benzene ( $\text{CH}_3\text{CH}_2\text{C}_6\text{H}_5$ ) [trace], 1,3-dimethyl benzene ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ ) [0.3], 1,4-dimethyl benzene ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ ) [0.075], 2-heptanone ( $\text{CH}_3\text{C}(=\text{O})(\text{CH}_2)_4\text{CH}_3$ ) [trace]

**System 3 Topcoat (Pratt and Lambert 785-637, -000, -118)**

Ethyl acetate ( $\text{CH}_3\text{CH}_2\text{OC}(=\text{O})\text{CH}_3$ ) [1.25], 2-pentanone ( $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$ ) [7.21], 4-methyl-2-pentanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_3$ ) [0.3913], butyl acetate ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(=\text{O})\text{CH}_3$ ) [1.04], ethyl benzene ( $\text{CH}_3\text{CH}_2\text{C}_6\text{H}_5$ ) [trace], 1,3-dimethyl benzene ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ ) [0.75], 1,4-dimethyl benzene ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ ) [0.2], 2-heptanone ( $\text{CH}_3\text{C}(=\text{O})(\text{CH}_2)_4\text{CH}_3$ ) [7.14].

**System 4 Primer (Deft 44GN36)**

nitroethane ( $\text{CH}_3\text{CH}_2\text{NO}_2$ ) [1.47], 2-butanol ( $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ ) [9.19]

**System 4 Topcoat (Pratt & Lambert 755-611/756-201)**

Three unidentified acetates, hexylacetate ( $\text{CH}_3(\text{CH}_2)_5\text{OC}(=\text{O})\text{CH}_3$ ) [1.25]

**System 6 Primer (Courtauds 513X423B)**

Methyl ethyl ketone (MEK,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ) [4.23], 2-pentanone ( $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$ ) [0.5], methyl benzene ( $\text{CH}_3\text{C}_6\text{H}_5$ ) [0.04], ethyl benzene ( $\text{CH}_3\text{CH}_2\text{C}_6\text{H}_5$ ) [0.09], 1,3-dimethyl benzene ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ ) [0.4], 1,4-dimethyl benzene ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ ) [0.12], 2-heptanone ( $\text{CH}_3\text{C}(=\text{O})(\text{CH}_2)_4\text{CH}_3$ ) [2.23], 2,6 dimethyl-4-heptanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_2\text{C}(\text{CH}_3)\text{HCH}_3$ ) [0.117].

**System 6 Topcoat (Courtauds MIL-C-85285)**

2-pentanone ( $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$ ) [1.3], 2-heptanone ( $\text{CH}_3\text{C}(=\text{O})(\text{CH}_2)_4\text{CH}_3$ ) [6.25], ethyl-3-ethoxypropionate ( $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-C(O)-O-CH}_2\text{CH}_3$ , EEP) [0.57]

**System 14 Primer (Spraylat EEAE145A/B)**

Methyl ethyl ketone (MEK,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ) [1.55], 4-methyl-2-pentanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_3$ ) [0.78], 2-heptanone ( $\text{CH}_3\text{C}(=\text{O})(\text{CH}_2)_4\text{CH}_3$ ) [0.89], ethyl-3-ethoxypropionate ( $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-C(O)-O-CH}_2\text{CH}_3$ , EEP) [0.06]

**System 14,15 Topcoat (Spraylat EUBG167 A/B)**

Methyl ethyl ketone (MEK,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ) [0.56], 4-methyl-2-pentanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_3$ ) [0.78], butyl acetate ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(=\text{O})\text{CH}_3$ ) [0.181], 2-heptanone ( $\text{CH}_3\text{C}(=\text{O})(\text{CH}_2)_4\text{CH}_3$ ) [0.89], 2,6 dimethyl-4-heptanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_2\text{C}(\text{CH}_3)\text{HCH}_3$ ) [0.39].

**System 15 Primer (Spraylat EEAE136A/B)**

Methyl ethyl ketone (MEK,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ) [3.94], 4-methyl-2-pentanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_3$ ) [5.09], 2-heptanone ( $\text{CH}_3\text{C}(=\text{O})(\text{CH}_2)_4\text{CH}_3$ ) [4.91], cyclohexanone ( $\text{C}(=\text{O})\text{C}_5\text{H}_{10}$  (*cyclo*)) [0.77], 2,6 dimethyl-4-heptanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_2\text{C}(\text{CH}_3)\text{HCH}_3$ ) [1.67].

**System 20 Primer (Deft 44-W-16)**

2-butanol ( $\text{CH}_3\text{C}(\text{OH})\text{HCH}_2\text{CH}_3$ ) [3.05], nitroethane ( $\text{CH}_3\text{CH}_2\text{NO}_2$ ) [5.57].

**System 20 Topcoat (Deft 55-GY-02)**

No detectable volatile organic species.

**MIL-P-23377G Type II Class C (Deft 02-GN-070)**

Methyl ethyl ketone (MEK,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ) [0.14], 2-pentanone ( $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_3$ ) [1.82], 4-methyl-2-pentanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_3$ ) [0.156], butyl acetate ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}(=\text{O})\text{CH}_3$ ) [0.04].

**System 23 Primer (US Paint K9800-K43)**

Methyl ethyl ketone (MEK,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ) [3.1], methyl benzene ( $\text{CH}_3\text{C}_6\text{H}_5$ ) [1.71], 2,6 dimethyl-4-heptanone ( $\text{CH}_3\text{C}(\text{CH}_3)\text{HCH}_2\text{C}(=\text{O})\text{CH}_2\text{C}(\text{CH}_3)\text{HCH}_3$ ) [0.57]

**System 23 Topcoat (US Paint K8032)**

Methyl ethyl ketone (MEK,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ) [4.79], ethyl acetate ( $\text{CH}_3\text{CH}_2\text{OC}(=\text{O})\text{CH}_3$ ) [0.452], 2-heptanone ( $\text{CH}_3\text{C}(=\text{O})(\text{CH}_2)_4\text{CH}_3$ ) [4.46], ethyl-3-ethoxypropionate ( $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-C(O)-O-CH}_2\text{CH}_3$ , EEP) [1.14], 1,3-dimethyl benzene ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$ ) [1.39], ethyl benzene ( $\text{CH}_3\text{CH}_2\text{C}_6\text{H}_5$ ) [0.452] .

**US Paint K1067-K45**

Methyl ethyl ketone (MEK,  $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$ ) [1.13], 2-heptanone ( $\text{CH}_3\text{C}(=\text{O})(\text{CH}_2)_4\text{CH}_3$ ) [0.892], ethyl-3-ethoxypropionate ( $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-C(O)-O-CH}_2\text{CH}_3$ , EEP) [0.114].

A summation of the **total** VOC g/L of paint is given in Table 2.

Table 2  
Total VOC for Coating Systems

<b>PAINT NAME</b>	<b>Total VOC g/liter of paint</b>
MIL-P-23377F t1cl1	12.07
TT-P-2760A	8.26
MIL-C-85285B	4.90
MIL-C-83286B	3.02
TT-P-2756	1.90
S 3 P&L724-500/01	2.67
S3 P&L 785's	17.78
S4 D 44GN36	10.66
S4 P&L 755's	3.65*
S6 C513X423B	7.72
S6C MIL-C-85285	8.12
S14SEEAE145A/B	3.28
S14,15 SEUBG167A/B	2.81
S15 SEEAE136A/B	16.38
S20 D44W16	8.62
S20 D55GY02	0
MIL-P-23377G TII CC D02GN070	2.61
S23 US K9800-K43	5.38
S23 US K8032	12.67
US K1067-K45	2.13

\* = contains unidentified acetates

## B. INCREMENTAL REACTIVITY OF COATING SYSTEMS

The following table contains the MIR values for the compounds observed in the coating systems:

Table 3

## Maximum Incremental Reactivity for Observed Coating VOCs

Compound Structure CAS #	Maximum Incremental Reactivity MIR <sub>VOC</sub> (g O <sub>3</sub> /g VOC)
Methyl ethyl ketone CH <sub>3</sub> C(=O)CH <sub>2</sub> CH <sub>3</sub> 78-93-3	1.18
4-methyl-2-pentanone CH <sub>3</sub> C(CH <sub>3</sub> )HCH <sub>2</sub> C(=O)CH <sub>3</sub> 108-10-1	0.85
cyclohexanone C(=O)C <sub>5</sub> H <sub>10</sub> ( <i>cyclo</i> ) 108-94-1	0.87
2-heptanone CH <sub>3</sub> C(=O)(CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> 110-43-0	0.75
2-pentanone CH <sub>3</sub> C(=O)CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> 107-87-9	0.99
5-methyl-2-hexanone CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> C(=O)CH <sub>3</sub> 110-12-3	0.75
2,6 dimethyl-4-heptanone CH <sub>3</sub> C(CH <sub>3</sub> )HCH <sub>2</sub> C(=O)CH <sub>2</sub> C(CH <sub>3</sub> )HCH <sub>3</sub> 108-83-8	0.6
isobutyl acetate (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OC(=O)CH <sub>3</sub> 110-19-0	1.1
butyl acetate CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OC(=O)CH <sub>3</sub> 123-86-4	0.67
ethyl-3-ethoxypropionate CH <sub>3</sub> CH <sub>2</sub> -O-CH <sub>2</sub> CH <sub>2</sub> -C(O)- O-CH <sub>2</sub> CH <sub>3</sub> 769-69-9	Between 1 and 3 Use 2.0 for calculations
ethyl acetate CH <sub>3</sub> CH <sub>2</sub> OC(=O)CH <sub>3</sub> 141-78-6	0.31
hexylacetate (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> OC(=O)CH <sub>3</sub> 142-92-7	0.8
1,4-dimethyl benzene CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> 106-42-3	6.6
methyl benzene CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> 108-88-3	2.7
1,3-dimethyl benzene CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> 108-38-3	8.2
ethyl benzene CH <sub>3</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> 100-41-4	2.7
nitroethane CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub> 79-24-3	~5
1-butanol CH <sub>3</sub> C(OH)HCH <sub>2</sub> CH <sub>3</sub> 78-92-2	2.7

There was only one compound for which the MIR value was not readily determined, nitroethane. Comparing nitroethane to other nitro-organic species, a value of approximately 5 was determined.

Using Equation (9) the following table is constructed:

Table 4  
MIR<sub>Coating</sub> for Each Coating System

<b>PAINT NAME</b>	<b>MIR<sub>Coating</sub> Σ(MIR<sub>VOC</sub> * [VOC]) (g O<sub>3</sub> / L paint)</b>
MIL-P-23377F t1c11	38.22
TT-P-2760A	9.00
MIL-C-85285B	5.62
MIL-C-83286B	3.81
TT-P-2756	1.60
S 3 P&L724-500/01	5.05
S3 P&L 785's	21.38
S4 D 44GN36	32.16
S4 P&L 755's	2.92*
S6 C513X423B	11.65
S6C MIL-C-85285	7.11
S14SEEA145A/B	3.28
S14,15 SEUBG167A/B	2.35
S15 SEEA136A/B	14.32
S20 D44W16	36.09
S20 D55GY02	0
MIL-P-23377G TII CC D02GN070	2.27
S23 US K9800-K43	8.62
S23 US K8032	24.04
US K1067-K45	2.23

\* = contains unidentified acetates

No concentration value for nitroethane was measured, because there was no system calibration. If a concentration value was determined, however, the coating systems' MIR<sub>Coating</sub> would only become larger.

Table 5

## Coating System Breakdown of Component MIR and Toxic Compounds

System #	Total MIR <sub>Coating</sub>	Primer	MIR <sub>Coating</sub>	Toxic ? (g/l) <sup>#</sup>	Topcoat	MIR <sub>Coating</sub>	Toxic ? (g/l) <sup>#</sup>
3	26.42	P&L 724/500's	5.04	0.845	P&L 785's	21.38	2.19
4	35.08	D 44GN36	32.16	9.19*	P&L 755's	2.92**	N
6	18.76	C 513X423B	11.65	4.88	MIL-C- 85285	7.11	N
14	5.63	S EEAE145	3.28	2.33	S EUBG167	2.35	1.34
15	16.68	S EEAE136	14.33	9.03	S EUBG167	2.35	1.34
17	1.60	-	-	-	D TTP 2756	1.6	N
20	36.09	D 44W16	36.09	3.05*	D 55GY02	0	N
23	32.68	US K9800	8.62	4.8	US K8032	24.04	6.64

\* = contains 2-butanol a compound on the toxic release inventory. \*\* = contains unidentified acetates. # = list in Section IV part B.

## C. OH RATE CONSTANT FOR ETHYL 3-ETHOXYPROPIONATE

Ethyl 3-ethoxypropionate ( $\text{CH}_3\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{-C(O)-O-CH}_2\text{CH}_3$ , EEP) is a volatile component of several coating systems. Neither its OH rate constant nor its atmospheric transformation products have not been previously measured, and are vital pieces of information for determining EEP's incremental reactivity. Using the techniques described previously, the EEP/OH rate constant ( $k_{\text{EEP}}$ ) is  $22.86 \pm 1.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Assuming an OH concentration of  $1 \times 10^6 \text{ molecules/cm}^3$ , the atmospheric lifetime ( $1/e$ ) of EEP is 12 hours. This rate constant is the average of the resultant rate constants determined using two reference compounds. Nonane as a reference [8] gave a  $k_{\text{EEP}}$  of  $22.68 \pm 1.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Figure 2) while

dodecane as a reference [8] resulted in a  $k_{\text{EEP}}$  of  $23.03 \pm 0.89 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Figure 3).

#### D. PRODUCT STUDIES OF ETHYL 3-ETHOXYPROPIONATE

The products of EEP have not been previously investigated, and this is the first known detailed investigation of the reaction products of EEP. Using the gas chromatography techniques described in previously, the atmospheric reaction products of EEP, at this time, are ethyl formate,  $\text{CH}_3\text{CH}_2\text{OC(O)H}$ , and an unknown product which is proposed to be  $\text{CH}_3\text{CH}_2\text{OC(O)CH}_2\text{CH}_2\text{OC(O)H}$  (Ethyl (3-formyloxy) propionate). The results of dinitrophenylhydrazine derivitazation (DNPH) yielded several transformation products. Acetaldehyde ( $\text{CH}_3\text{C(=O)H}$ ), Ethyl (2 formyl) acetate ( $\text{HC(=O)CH}_2\text{C(=O)OCH}_2\text{CH}_3$ ), ethyl glyoxalate ( $\text{HC(=O)C(=O)OCH}_2\text{CH}_3$ ) have been tentatively identified as the aldehyde and ketone products. The observed products account for approximately ~90% of EEP reacted. This data support the mechanism shown in Figure 4. The toxicological properties of these transformation products are not known at this time.

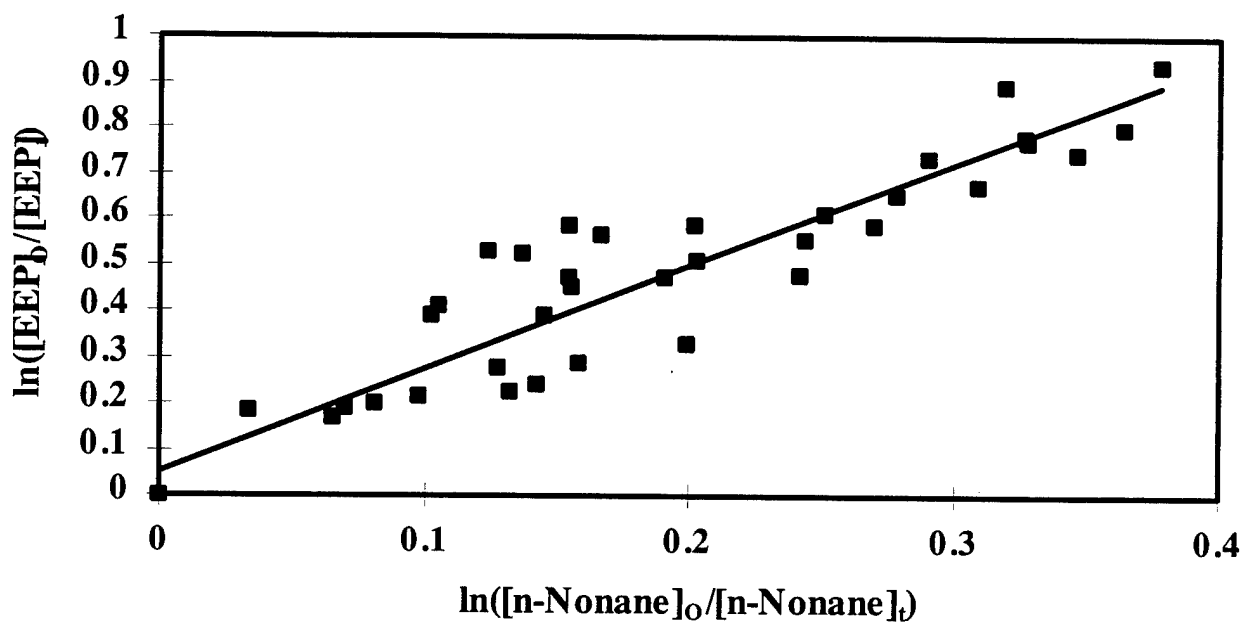


Figure 2. Plot of Reaction (6) using n-nonane as a reference for OH + EEP. Using a value of  $10.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $k_{n\text{-nonane}}$ ,  $k_{\text{EEP}}$  is  $22.68 \pm 1.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

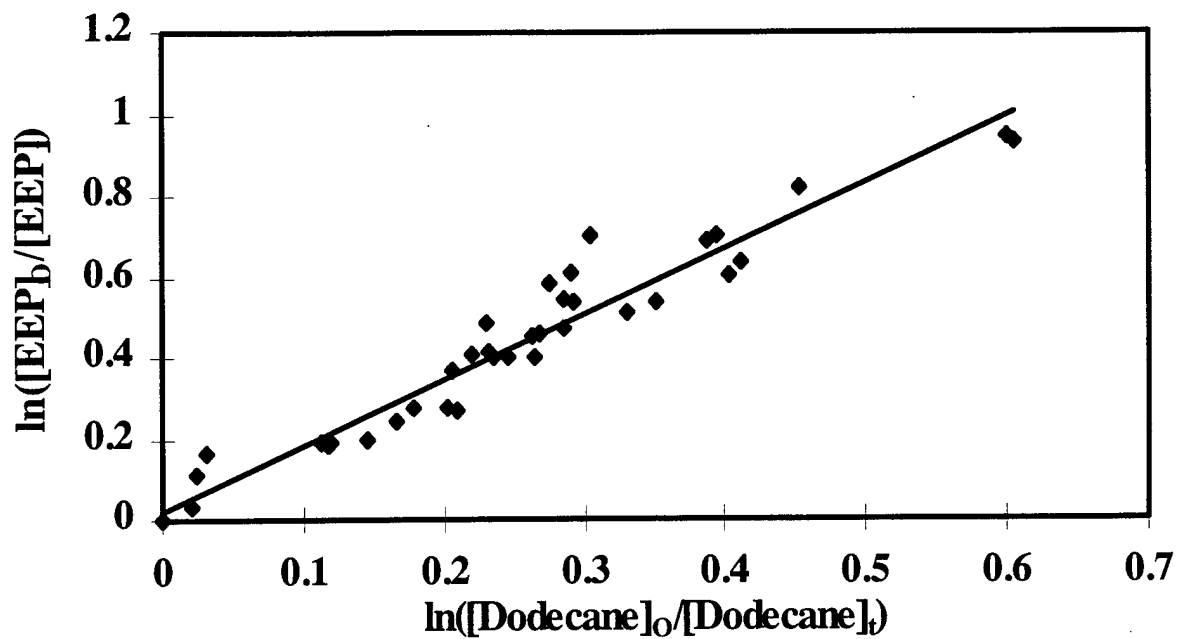


Figure 3. Plot of Reaction (6) using dodecane as a reference for OH + EEP. Using a value of  $14.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for  $k_{\text{dodecane}}$ ,  $k_{\text{EEP}}$  is  $23.03 \pm 0.89 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

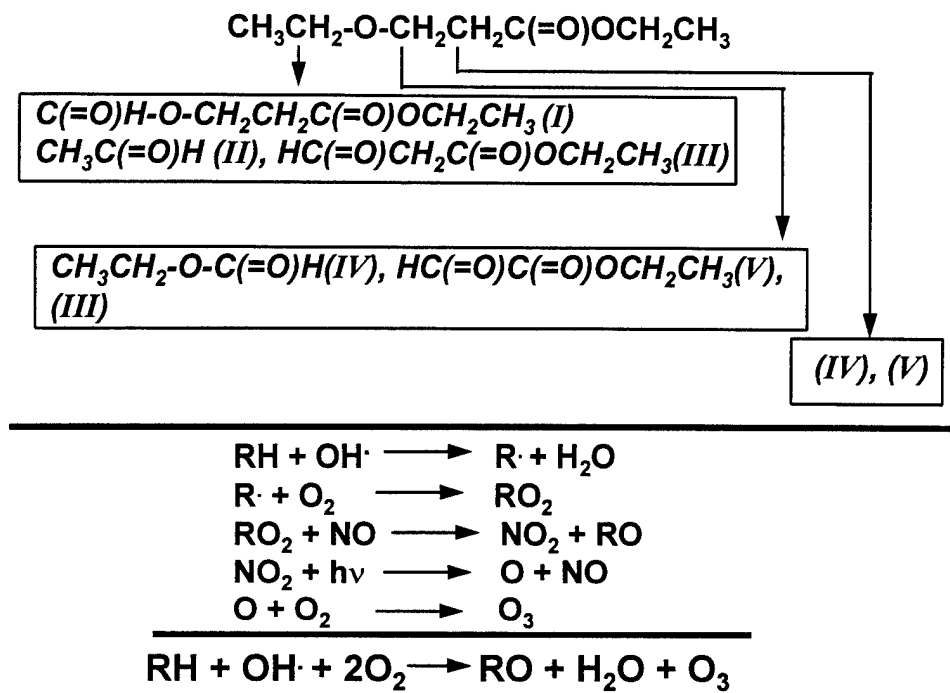


Figure 4. Atmospheric transformation mechanism for ethyl-3-ethoxypropionate with  $\text{O}_3$  formation mechanism.

## SECTION IV

### DISCUSSION

#### A. COMPARISON OF [VOC] VS. INCREMENTAL REACTIVITY OF COATING SYSTEMS

The comparison of Tables 2 and 4 yields interesting observations. The  $MIR_{Coating}$  ( $\Sigma(MIR_{VOC} * VOC)$ ) for most coating systems has almost the same value as Total VOC. The large discrepancies occur for the coating systems that contain the aromatics *m*-xylene, ethyl benzene, *o*-xylene, methyl benzene and 2-butanol. From the rest of the coating systems a simple formula of Total VOCs  $\cong MIR_{Coating}$  works well. The general conclusions are that the more VOCs a coating emits the higher its  $MIR_{Coating}$  value and the average  $MIR_{VOC}$  for "typical" coating components is around 1.0. One coating, Deft 55GY02, showed no VOC emissions with the sampling system used.

#### B. COMPOUNDS OF SIGNIFICANCE FOR TOXICOLOGICAL IMPACT

The following compounds have been listed as hazardous air pollutants (HAPs) by the Environmental Protection Agency in the 1990 Clean Air Act Amendments (CAAA):

4-methyl-2-pentanone (methyl isobutyl ketone)

ethyl benzene

methyl benzene (toluene)

methyl ethyl ketone

xylene(s)

These compounds can affect the central nervous system and cause eye and mucous membrane irritation. The solvent, 2-butanol, is a toxic release inventory (TRI) chemical

meaning its emissions have to be reported, but it is not yet a HAP. There were only two coatings (Deft 44GN36 and Deft 44W16) that contained 2-butanol.

### C. ATMOSPHERIC MECHANISM OF ETHYL-3-ETHOXYPROPIONATE

The atmospheric transformation mechanism in Figure 4 highlights the complicated reaction pathways possible for VOC. Depending on where the OH radical hydrogen abstraction occurred on the molecule, a an entirely different set of reaction products were observed. One important point to note is that a pattern is emerging regarding the reactive sites of oxygenated organics. As seen in 2-ethoxyethyl acetate [9], the most significant site for OH attack are the methylene groups (-CH<sub>2</sub>-) connected to ether oxygens resulting in aldehyde, ketones or formate products.

## SECTION IV

### CONCLUSIONS

Coating systems typically have a complex emission profile. This profile was found to be inaccurately represented by the Material Safety Data Sheets (MSDSs), and the speciation and quantification of coatings emissions presented in this report offer a more detailed picture. Using the unique combination of GC/FTIR/MS the most volatile compounds, and hence the most atmospherically important, can be identified and quantified. But, an understanding of each VOC's atmospheric impact is necessary in order to accurately assess the atmospheric impact of a particular coating system. The blending of incremental reactivity with the emission analysis resulted in a determination of the ozone-forming potential of each coating system.

The atmospheric reaction kinetics and products of one paint component, EEP, have been investigated in detail. Significant new insights into the atmospheric chemistry of paint components were gleaned from these results. The methylene groups (-CH<sub>2</sub>-) connected to ether oxygens are significantly more reactive than the other CH groups. These important new discoveries were used to determine the incremental reactivity of EEP as it is released into the atmosphere and to determine EEP's atmospheric mechanism.

This new and vital information will be used to direct the research of the atmospheric assessment program.

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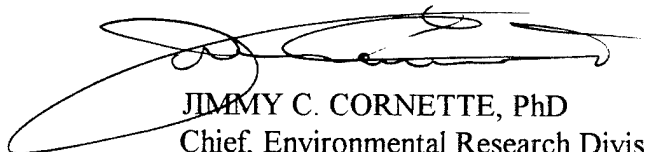
This technical report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for publication.

FOR THE COMMANDER:



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