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INHALATION TOXICOLOGY: III. EVALUATION OF THERMAL DEGRADATION PRODUCTS FROM AIRCRAFT AND AUTOMOBILE ENGINE OILS, AIRCRAFT HYDRAULIC FLUID, AND MINERAL OIL

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NOTICE

The animals used for this experiment were lawfully acquired and treated in accordance with the "Guide for the Care and Use of Laboratory Animals" prepared by the Committee on Revision of the Guide for Laboratory Animal Facilities and Care of the Institute of Laboratory Animal Resources, National Research Council, DHEW Publication No. (NIH) 74-23.

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| 16. Abstract | | | | |
| A malfunctioning seal in the | ne gear-reduct: | ion box of a turbo | prop aircraft | engine |
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| from aircraft lubricating oils and some related products. Rats were exposed smoke from these products and relative toxicity evaluated in terms of time-t incapacitation and time-to-death. The carbon monoxide (CO) content of the s | | | | |
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| was the basis for concludi | | - | • | - |
| any chemical species, othe | | | | |
| total toxicity. | | | | |
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INHALATION TOXICOLOGY: III. EVALUATION OF THERMAL DEGRADATION PRODUCTS FROM AIRCRAFT AND AUTOMOPILE ENGINE OILS, AIRCRAFT HYDRAULIC FLUID, AND MINERAL OIL

BACKGROUND

The turbine-powered, propeller-driven (turboprop) aircraft is a popular configuration, especially in the pressurized, medium-sized, twin-engined, business category. This efficient and economical power plant is supplied in at least one version by most major power plant manufacturers and is used on a variety of aircraft. The combination represents, therefore, a sizabable and important segment of the commercial fleet of aircraft.

In 1981 it became a matter of some concern that several unexplained crashes of these turboprop aircraft might possibly be due to pilot incapacitation from toxic fumes (1,2). It was suggested that such fumes could originate in the turboprop power plant and be introduced into the cabin through the bleed air that is taken from the turbine's compressor and used to pressurize the aircraft.

One accident involving a turboprop twin-engined aircraft was investigated to the extent that both engines were recovered from the lake in which the aircraft had crashed. One operational engine was assembled from the parts of the two engines and tested in the aeronautical engineering department of a west coast university. Samples of compressor bleed air from this engine were collected and chemically analyzed.

From this and other studies it has been alleged that a broken carbon seal in the engine will allow lubricating oil to enter the compressor section; that the resulting oil-contaminated bleed air will enter the cabin; and that there are present in this bleed air toxic substances that can and will degrade pilot performance or even incapacitate aircraft occupants.

As a result of such allegations and the ensuing rumors, the National Transportation Safety Board (NTSB) reviewed the accident statistics for this type of aircraft. They concluded that the frequency and the nature of the accidents justified additional tests of the quality of the bleed air. The test hypothesis was that the bleed air contained some substance that was toxic to the aircraft operator when inhaled.

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A particular combination of aircraft and turboprop power plant that had been mentioned prominently in the news media coverage was the Mitsubishi MU-2 equipped with Garrett Turboprop Engine Company TPE-331 engines. Therefore, during the period July 12-25, 1981, a series of tests was conducted at the Garrett facilities using a TPE-331 mounted on a test stand. For the tests, the engine was operated under various conditions, including the intentional introduction of known amounts of its lubricating oil (Exxon 2380 Jet Engine Oil) directly into the air intake of the engine. Aliquots of compressor bleed air were collected by several sampling techniques and subjected to chemical analysis in three different participating laboratories. Additional online analyses were conducted at the site. The results of all these tests are to be published by the NTSB (3).

The online analytical chemical results from the bleed air analyses did not support the hypothesis that harmful concentrations of carbon monoxide (CO), carbon dioxide, or oxides of nitrogen were present. Analysis of the batch samples, using a gas chromatograph/mass spectrometer, revealed the presence of a number of identifiable gases, but these were reported to be present in such low concentrations that they probably would not alter a pilot's perception or behavior. However, the presence of an unidentified substance of exceptional toxicity (e.g., more toxic than CO) emanating from the engine could not be ruled out.

Furthermore, these NTSB-sponsored tests showed that when oil was injected directly into the engine air intake it appeared as a mist in the bleed-air line, but this mist was removed by glass wool filters ahead of the sampling/analytical devices. It was possible, therefore, that with an unfiltered line a significant toxicity could be associated with breathing the oil mist.

INTRODUCTION

Any attempt to assess the combined toxicity of a mixture of unknown chemical compounds by doing only a chemical analysis is an open invitation for utter frustration. Only those compounds for which the selected analysis is appropriate will be quantitated and, even though several potentially toxic species are measured, it is at present almost impossible to predict the combined toxic expression of such a mixture.

It was principally for these reasons that we decided to use experimental animals to investigate the toxicity of acute exposures to the thermal decomposition products (TDP) of Exxon 2380 and other lubricants, as well as the toxicity associated with inhalation of oil aerosols. The foundation and basic techniques for such inhalation toxicology assays are well established and have been in continual use in our laboratory for the past 10 years. With this technique, the exposed animal serves as both the "analyzer" and the "integrator," assuring that each toxic species, known and unknown, will not only be accounted for but will be assigned its proper weighting factor in summing the total effective toxicity of the mixture.

Two types of animal experiments were designed and carried out in the Aviation Toxicology laboratories of the Civil Aeromedical Institute in Oklahoma City, Oklahoma.

The first set of experiments would expose rats to the TDP from synthetic and petroleum-based lubricants and from one fire-resistant hydraulic fluid used in aircraft systems. The TDP would be generated at specific temperatures over the range 300° C to 600° C and include both flaming and nonflaming decomposition. Measured physiological endpoints would be time-to-death (t_d) and time-to-incapacitation (t_i).

The measurement of CO production throughout the exposure period would give an estimate of the total toxic dose due to CO. Our experience with CO studies in rats should allow a reliable judgment of whether or not a component is produced that contributes more to the total toxicity than does CO.

A second set of experiments would involve a 7-hour exposure of both rats and chickens to aerosols of one synthetic lubricant and of a chemical grade of light paraffin oil. These animals would be kept for a minimum of 35 days postexposure and be observed daily for any signs of toxicity.

MATERIALS AND METHODS

Test Animals. Male rats (Sprague-Dawley derived) were obtained from Charles River Breeding Laboratories, Wilmington, Massachusetts; their size was 100 to 120 g when acquired. All animals were held in isolation for 8 days, and, as an added precaution, maintained during the first 4 days on drinking water that contained 1.5 g sulfathiazole per liter. After the 8-day period they were moved from isolation into regular quarters. All animals to be used on a given day were fasted overnight; each was weighed just prior to exposure.

Test Materials. A total of nine materials was utilized in the testing program. Six of these were synthetic lubricating oils, one was a petroleumbased lubricating oil, one a synthetic hydraulic fluid, and the last was a refined paraffin oil. These materials and their specific gravities are in Table 1.

Four of the synthetic lubricants were products of Exxon Company, Houston, Texas. Three of these were different batch numbers of the same turbine oil product, identified as Exxon 2380. Test specimens of batch numbers B193 and B227 were taken from freshly-opened 1-quart cans of Exxon 2380. The test specimen, Exxon 2380 (batch 245), was oil that had been used in an operating turboprop aircraft for 165 hours. The fourth test specimen was taken from a freshly-opened 1-quart can of Exxon 2389 (batch 64); this particular formulation is used in some aircraft in the Federal Aviation Administration (FAA) fleet.

Two synthetic lubricants were products of Mobil Oil Corporation, New York, New York. Mobil II Jet Oil is a product also used in some FAA turboprop aircraft. The second product, Mobil I, is a synthetic oil formulated for use in automobile piston engines. An additional automobile motor oil, Quaker State 10W-40HD (Quaker State Oil Refining Corporation, Oil City, Pennsylvania), was tested for comparison of a petroleum-based oil with the synthetic Mobil I product. All three test specimens were taken from freshly opened l-quart cans.

On previous occasions, and in connection with other aircraft accidents unrelated to any potential bleed-air problem, the question of toxicity of TDP from hydraulic fluid had arisen. Therefore, we took this opportunity to evaluate also a sample of synthetic hydraulic fluid that is reported to exhibit improved thermal stability properties. The test specimen was Skydrol 500B Fire-Resistant Hydraulic Fluid (Monsanto Company, St. Louis, Missouri) and came from a previously-unopened l-quart can.

| Material | Density (g/mL) | Wt of 3-mL Sample (g) |
|--|-------------------|--------------------------|
| Exxon Turbo Oil 2380 (B193) | 0.9512 | 2.8536 |
| Exxon Turbo 0il 2380 (B227) | 0.9462 | 2.8386 |
| Exxon Turbo 0il 2380 (B245), Used | 0.9456 | 2.8368 |
| Exxon Turbo 0il 2389 (B64) | 0.9208 | 2.7624 |
| Mobil II Jet Oil | 0.9676 | 2.9028 |
| Mobil I Synthetic Motor Oil | 0.8501 | 2.5503 |
| Quaker State 10W-40 HD Motor Oil | 0.8536 | 2.5608 |
| Skydrol 500B Fire-Resistant Hydraulic Fluid | 1.0372 | 3.1116 |
| Paraffin Oil* | 0.8404 | 2.5212 |

Table 1. Test Materials

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*Fisher Scientific Company, Fair Lawn, New Jersey.

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Exposure Chamber/Combustion Assembly. The exposure chamber used in this study, as well as the peripheral analytical, oxygen replenishing, and combustion equipment, have been described in detail in previous publications (4,5). The spark ignition assembly described in those references was replaced by a simple hot-wire igniter for these experiments. The apparatus and component sources are shown in Figure 1.



Figure 1. Combustion/Exposure Assembly

- 1. Gearmotor, Model 3M126, 6 rpm, 1/20 hp; Dayton Manufacturing Company, Chicago, IL.
- 2. Animal Exposure Chamber
- Heating Unit, Model NV2X6, 425 W at 57.5 V, semicylindrical; Watlow Electric Manufacturing Company, 12001 Lackland Road, St. Louis, MO.
- 4. Same as No. 3
- 5. Thermocouple, chromel-alumel; Omega Engineering Inc., Stamford, CT.
- 6. Hot Wire Igniter
- 7. Combustion Tube
- 8. Combustion Boat
- 9. Spring Clamp
- 10. Smoke Detector

Internal dimensions of the polymethylmethacrylate (PMMA) chamber were 25.4 cm long, 22 cm wide and 22 cm high; the three-compartment rotating cage was 20 cm in diameter and 21.4 cm long. The quartz (Vycor) combustion tube consisted of a section 5 cm in diameter, 33 cm long, connected to an 8 cm long, 2.5 cm in diameter section by a 6.4 cm taper segment. The total enclosed volume for the chamber, combustion tube, and recirculation assembly was 12.6 L.

Heat was applied to the oil sample with two semicylindrical heating elements encircling the 5 cm diameter section of the combustion tube. A chromel-alumel thermocouple embedded in the lower element was calibrated against a similar thermocouple in the sample combustion boat to provide a reference temperature for sample thermal control. Liquid test samples were contained in semicylindrical quartz combustion boats with closed ends, 7.5 cm long x 4 cm wide. Ignition of gases evolved from the heated oil samples was accomplished, when desired, with a hot-wire igniter consisting of two loose coils of resistance wire suspended between heavy stainless steel wires that extended down the tube to a point slightly downstream from the combustion boat. Current was applied to the igniter from a 12 volt wet cell battery from the time of sample insertion until gases from the sample ignited.

Aerosol Exposure Assembly. All aerosol exposures were performed in a PMMA chamber with inside dimensions 75 cm long x 61 cm wide and 45 cm high, and an internal volume of approximately 205 L. Bushings were installed along one side to accept three rat holders for head-only exposures. Each holder was constructed from a 21 cm length of 6.5 cm diameter PMMA tubing equipped with leg holes, an adjustable sliding plug, and a plastic restraining collar; the end of the holder that protruded into the chamber was fitted with a rubber seal encircling the rat's neck and preventing any body exposure to gas or aerosol. An end face of the chamber contained two openings, 8.9 cm in diameter, in diametric corners. Aerosols were produced by flowing compressed air through a 250-mL glass atomizer containing the test liquid. The atomizer was positioned at the top corner opening and the lower opening was fitted with a plastic tube that terminated in a fume hood; this arrangement allowed a flow-through type of atmosphere generation. Chamber mixing fans were not used in this study to avoid excessive contact of the aerosol with the walls of the chamber.

Head-only chicken exposures required a different restraining system due to the different body configuration. Each animal was placed in a container made from a 400-mL disposable plastic beaker trimmed to the 340-mL line; a sheet of thin rubber (dental dam material) with a 1.9 cm hole in the center was placed over its head and secured to the beaker with a large rubber band. Then a second X-shaped collar of 2 mm thick gum rubber with a 2.5 cm hole in the center was fitted over the chick's head, folded over the sides of the beaker, and taped in place. The dental dam provided a soft but airtight seal around the bird's neck and the heavier rubber collar prevented escape.

Animal Exposure Procedures

Combustion Products. Sequentially, the exposure procedure consisted of bringing the furnace to the desired temperature, weighing the rats, and placing them in the individual compartments of the rotating cage. The chamber was closed and the recirculation and combustion equipment attached. The air pump, which circulated chamber atmosphere through the gas chromatograph's sample loop, was activated and the chamber mixing blower and fan turned on. A 3-mL sample of the fluid to be tested was pipetted into the quartz combustion boat. For flaming combustion experiments, the hot-wire igniter was turned on; for nonflaming experiments, the igniter was removed from the assembly. Simultaneously, the sample was pushed into the heated area of the combustion tube, cage rotation was begun, the system sealed, and the recirculation blower and sampling timer were activated.

The chamber atmosphere was sampled and analyzed for 0_2 and CO at 1.88-min intervals, beginning 1 min after insertion of the sample. Rats were observed until they could no longer perform the coordinated act of walking in the rotating cage and began to tumble; cage rotation was then stopped and t_1 was recorded. The t_d was recorded when visible signs of breathing ceased. Oxygen was replenished to ambient levels when necessary, as indicated by the gas chromatographic analysis. The exposure time was 30 min except in a few experiments where the CO concentrations were very low; in these cases exposure time was extended in order to determine a reaction time. Any surviving animals were held for observation for a minimum of 14 days.

<u>Aerosols</u>. Rats were weighed and placed in the individual head-only holders; these were then fitted into the bushings on the side of the 205-L chamber so that the rats' heads protruded into the chamber interior.

Chickens, for head-only exposures, were placed in the plastic beakers and secured by the rubber seal and restraining collar. For whole-body exposures, chickens were simply placed in the chamber and allowed to move about freely.

With the experimental animals in place, the test material was added to the atomizer and the entire assembly weighed to the nearest 0.01 g. (Samples of used oil were first filtered through "Shark Skin" filter paper (Arthur H. Thomas Co., Philadelphia, Pennsylvania) to prevent clogging the atomizer.) The atomizer was clamped in position and connected to a tank of compressed air through a pressure regulator and a flowmeter. The regulator was used to control the airflow to the atomizer at a constant 32 cfm (15.1 L/s) throughout the 7-hour exposure period. Timing began when the airflow started.

At the end of the exposure, airflow was stopped, animals were removed and held for observation, and the atomizer assembly was reweighed to determine the quantity of fluid used.

RESULTS AND DISCUSSION

The thermal stability of the product of primary interest, Exxon 2380 (B193), was evaluated in a preliminary experiment with no animal exposure. A small sample was placed in the furnace boat of the combustion assembly and the furnace temperature raised slowly. Traces of condensation first appeared downstream at 208°C; measurable CO occurred at 306°C along with a dramatic increase in smoke density; CO evolution then increased rapidly,

producing a chamber concentration of 5,000 ppm at 344° C. By 350° C most of the sample was reduced to a solid char that continued to evolve CO until a chamber concentration of 10,600 ppm CO was attained at a furnace temperature of 533° C.

The second se

This preliminary experiment established 300° C as a suitable lower limit for the next series of tests.

Thermal Decomposition/Animal Exposure Tests

Exxon 2380 decomposition at a selected set of nonflaming isothermal conditions gave the results in Table 2. At 300° C the amount of CO produced was quite low and there was no visible effect on the animals during the 30-min exposure. At 350° C, the first experiment was terminated at the scheduled 30 min; no incapacitation occurred. It was obvious, however, that these animals were approaching incapacitation; therefore, a second run was conducted at 350° C and continued until all three animals had expired. The data from this second run are presented in the table. The data for the experiments at 375° C and 600° C are the averaged values from two runs at each temperature.

As the isothermal decomposition temperature was increased (from experiment to experiment), the production of CO began earlier and proceeded faster. The animal response times, t_i and t_d , became correspondingly shorter and are therefore inversely related to the furnace temperature. Table 2 also contains the maximum CO concentration produced at each temperature.

The integrated area under a plot of CO concentration versus exposure time, i.e., Ct-product (ppm-min), was calculated for each individual animal from the beginning of exposure up to the two response times. This value, presented as the average for all animals in experiments conducted at a single temperature, represents a quantity that is related to the "dose" of CO that t^{+} animal could have received up to the time of incapacitation (Ct_i) or death (Ct_d).

In previous studies of exposure to CO alone, we have found these values to be relatively constant--around 25,000 to 35,000 for Ct_i and 70,000 to 90,000 for Ct_d . In CO-containing atmospheres that also contain irritating components, the Ct-products (for CO) increase with increasing irritant concentration; this is explained by the experimentally documented fact that respiratory rate and minute-respiratory-volume both decrease when irritants are present. This effect of irritants always increases Ct_i more than Ct_d .

On the other hand, when a second toxic gas is present in significant concentrations along with CO, the Ct-products for CO are always less than for the case of CO alone. We, therefore, conclude that the <u>major</u> toxic component of the TDP from Exxon 2380 is carbon monoxide.

The comparison of new Exxon 2380 with a batch that had been drained from an aircraft engine after 168 hours' use is shown in Table 3. Each material was tested at three temperatures under both flaming and nonflaming

| 2380 (B193) | Combustion Mode |
|--|---|
| Table 2. Rat Response to Decomposition Products of Exxon 2380 (B193) | Generated at Different Temperatures, Nonflaming Combustion Mode |

| | | A | Animal Response Times | sponse T | imes | | Carbo | Carbon Monoxide | le | |
|-------------------------------|-------------------|-------------------------|----------------------------------|----------------------------|----------------------------------|---------------|---------------------------------------|---|-----------------------------------|------------------|
| Temperature ^o C | Number Exposed | t _i , ave | t ₁ , min ave (sd) | t _d , mj ave | t _d , min ave (sd) | C, max ppm | <u>Integra</u> Ct _i , a | Integrated Ct-product, ppm-min Ct ₁ , ave (sd) Ct _d , ave (sd) | coduct, I Ct _d , av | pm-min e (sd) |
| 300 | £ | NR* | * | 2 | NR | 1,040 | NR | | NR | |
| 350 | £ | 41.5 | 41.5 (0.23) | 53.7 | (0.58) | 2,400 | 56986 | (512) | 85178 | (1382) |
| 375 | 9 | 13.2 | 13.2 (0.34) | 15.5 | (0.63) | 14,300 | 46442 | (5514) | 79673 | (8184) |
| 400 | e | 8.8 | 8.8 (0.31) | 10.3 | (0.21) | 20,900 | 49722 | (5953) | 79936 | (4306) |
| 600 | 6 | 4.8 | 4.8 (0.39) | 7.2 | (1.24) | 17,000 | 44963 | (7458) | 85358 | (20469) |
| | | | | | | | | | | |

*At 300°C, no response was noted during the 30-min exposure period

Table 3. Rat Response to Decomposition Products of New and Used Exxon 2380* at Three Temperatures

(1382) (8184) (8076) (26367) (31381) (18897) (ps) Integrated Ct-product, ppm-min Ct_d, ave 85178 101082 88344 79673 92541 134975 Carbon Monoxide (111) (5514) (4455) (512) (1131) (ps) (12101) Ct_i, ave 56986 50153 83922 46442 36460 41933 14,300 14,400 13,400 2,400 1,850 15,500 C, max mdd (2.24) (ps) (0.58) (5.58) (0.63) (2.16) (2.01 t_d, min ave (s Animal Response Times 53.7 67.9 15.5 17.1 10.1 12.7 (96.9) (0.34) (0.77) (0.23) (0.37) (0.33)(ps) t_i, min ave 41.5 65.4 13.2 13.5 5.7 5.3 Rats No. m ĉ Q Q و و New/ Used Used Used Used New New New Mode** NF NF NF NF FL FL Temp. °C 350 350 375 375 400 400

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*New Exxon 2380 was from batch 193; used Exxon 2380 was from batch 245 with 168 hours total time in use. **NF = nonflaming; FL = flaming mode.

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conditions. For only one of the pairs of test parameters is the difference between new and used oil statistically significant. In the 400° C flaming mode, the difference in Ct-product is significant at the p=0.05 level (Student t-test, 2-tailed). Even here, however, the times-to-death are not significantly different. We conclude, therefore, that used oil does not contain or produce TDP's that are significantly different from those generated by new oil--in either a qualitative or a quantitative sense.

The results of comparisons made between Exxon 2380 and some related contemporary products are in Table 4. Each material was tested at 400° C, under flaming and nonflaming conditions. It is apparent that there are some significant differences in rat response times and in CO production, both among the different materials and between the flaming/nonflaming modes for some of the individual materials. At the p=0.05 level (Student t-test, 2-tailed), the t_i's are different (flaming vs. nonflaming) for all materials except the Quaker State Oil. Conversely, only for Quaker State oil are the two t_d's different. The Ct-products for both incapacitation and death are not significantly different when flaming is compared with nonflaming mode. The aviation hydraulic fluid, Skydrol 500B, does not decompose appreciably at 400°C unless it is flaming (400°C is obviously below its autoignition temperature); this explains the lack of response in the 400°C nonflaming test.

When the response times listed in Table 4 are arranged in the order of increasing t_i , it is easier to compare the relative potential toxicities. Table 5 presents the seven materials in the order of decreasing toxicity (as implied by increasing magnitude of t_i) for flaming and nonflaming modes. This table also presents the "worst-case" rank order, in which a material's position is determined by using the t_i that is the shorter of the two obtained from flaming and nonflaming tests.

When ranked by t_i in the 400°C nonflaming mode, it is interesting that the four aviation products are the four least-toxic materials. The 400°C flaming data, when compared to nonflaming, illustrate a common phenomenon in combustion toxicology: the rank-orders for the same set of materials in the two modes are quite different. The least-toxic, nonflaming, becomes the most-toxic material under flaming conditions. Also, the two materials that are now least toxic, in the flaming mode, are the two that are, or are derived from, natural petroleum products; the others are all synthetics.

The most important distinction between the flaming/nonflaming rank orders is the fact that the position of Skydrol changed from <u>least</u> toxic (nonflaming) to most toxic (flaming). This complete turnabout has not been an unusual occurrence in the 10-year period that this laboratory has been testing materials, and it serves to emphasize the potential folly of selecting and/or specifying a single thermal environment at which all materials would be evaluated.

Our philosophy that has emerged from our testing experience is that, ideally, materials should be evaluated for toxicity over the range of thermal environments that they might reasonably encounter in a "real" fire,

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Table 4. Rat Responses to Decomposition Products from Exxon 2380 (B193) and Related Products at $400^{\circ}\mathrm{C}$

(ps) (1244) (4306) (12370) (24096) 31381) (2217) (11862) (36424) (23068) (27795) (6113) (10827) (29917) Integrated Ct-product, ppm-min *Response times are the means of three animals except for Exxon 2380 (B193) FL for which n = 6. Ctd, ave 79936 92491 108032 107862 92541 96523 95574 129156 103548 147126 116053 138694 (4822) 86945 (3852) (2913) (926) (ps) (874) (2642) (7131)(12871) (5953) (19269) (1222) (1250) (12412)Carbon Monoxide Cti, ave 61220 48618 41116 51253 48315 49138 64300 54489 49722 36460 47617 39687 48297 17,300 19,500 14,200 15,40014,00012,500 9,200 21,500 10,200 16,700 13,400 580 20,900 C, max mdd (0.21)(2.16) (0.71) (2.54) (0.59) (2.45) (ps) (1.62) (0.59) (0.12) (0.87) (0.10)(6.53) 7.0 (1.55) t_d, min ave (s Animal Response Times* RR 8.3 17.3 9.4 9.1 12.7 23.7 12.8 10.3 13.1 (0.31)(0.37)(1.12) (0.12) (0.21)(0.06) (0.10)(2.06) (0.10)(0.47) 4.6 (0.30) (0.50)(0.20 (ps) NR*** t_i, min ave (sd 5.6 8.8 8.8 6.1 6.5 5.2 10.4 6.2 8.0 10.7 Mode** FL FL NF FL FL NF FL FL FL FL NF FL Exxon 2380 (B193) Mobil II (Jet) Skydrol 500B Paraffin 0il QS 10W-40HD Exxon 2389 Material Mobil I

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**NF = nonflaming; FL = flaming.

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the 30-min exposure; no deaths occurred among the exposed animals during the 14-day postexposure ***NR = no response. Skydrol 500B, in the nonflaming mode, did not incapacitate any of the rats during observation period. Ranked Incapacitation Times (t $_{\rm i})$ for Decomposition Products Evolved at $400^{0}{\rm C}$ Table 5.

| Nonflaming (400 ⁰ C) | ~C) | Flaming (400°C) | | Worst Cas | Worst Case (400 ⁰ C) | |
|---------------------------------|-----------------------|------------------|----------------------|------------------|---------------------------------|----------------------|
| Material | t _i (min)* | Material | t _i (min) | Material | Mode*** | t _i (min) |
| Paraffin Oil | 5.6 | Skydrol 500B | 4.6 | Skydrol 500B | FL | 4.6 |
| Mobil I | 6.5 | Mobil I | 5.2 | Mobil I | FL | 5.2 |
| Quaker State | 8.0 | Exxon 2380(B193) | 5.7 | Paraffin Oil | NF | 5.6 |
| Exxon 2380(B193) | 8.8 | Exxon 2389 | 6.1 | Exxon 2380(B193) | FL | 5.7 |
| Exxon 2389 | 8.8 | Mobil II (Jet) | 6.2 | Exxon 2389 | FL | 6.1 |
| Mobil II (Jet) | 10.4 | Paraffin Oil | 7.5 | Mobil II (Jet) | FL | 6.2 |
| Skydrol 500B | NR** | Quaker State | 10.7 | Quaker State | NF | 8.0 |

*Mean t_i , refer to Table 4 for number of animals and standard deviations when comparing the significance of any pair of values.

**NR = no response during the 30-min exposure period.
***FL = flaming; NF = nonflaming.

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then be rank-ordered according to the shortest t_i that was obtained. This we have referred to as the "worst-case" approach. The third rank-ordering presented in Table 5 is based on such a philosophy. For each material there is presented the shorter of the two t_i 's obtained and the combustion mode (FL or NF) for which that response time was produced.

In this listing by worst-case performance, Exxon 2380 again appears at midrange, Skydrol is most toxic, and Quaker State least toxic. We see again that five of the seven materials generated their more toxic atmospheres under flaming conditions, but for Quaker State and paraffin oils the more toxic smoke was produced with nonflaming thermal decomposition.

All of the experiments that exposed rats to aerosol atmospheres of three of the materials (new and used Exxon 2380, paraffin oil) gave essentially negative results. Each group of three rats was exposed for 7 hours, during which time a total weight of lubricant that ranged from 47.2 g to 48.5 g was aerosolized into the chamber airflow. The particle size range of the aerosols was not measured; it ranged, however, from heavier droplets that settled rapidly, and were available only briefly for inhalation, to extremely fine particles that remained suspended much longer. Therefore, the actual fraction of generated aerosol that was inhaled cannot be reliably estimated.

None of the exposed rats seemed to be adversely affected at the end of the 7-hour exposure, and all exhibited normal behavior and weight gain during the 40-day postexposure observation period. At autopsy no gross abnormalities were found.

The aerosol exposure using chickens was limited to a single 7-hour test with used Exxon 2380 and a 7-hour sham exposure with no aerosol to evaluate the effects of the restraining system. Each test utilized six chickens: three in "head-only" restrainers and three that were unrestrained. None of the exposed animals were incapacitated in 7 hours; all behaved normally during postexposure observation.

CONCLUSIONS

It is widely recognized among combustion toxicologists that the exact nature of the thermal decomposition products from any material is dependent on the manner in which thermal degradation is accomplished. Therefore, the reported results, strictly speaking, apply to these materials only for the thermal environments that were utilized in these tests.

We feel, however, that the nonflaming mode, especially at the 400° C temperature, is an adequate model of thermal degradation in the turboprop engine. The results obtained under flaming conditions, on the other hand, would be applicable to a spillage situation (e.g., an accident) in which such materials are freely burning (flaming).

Based on the results obtained from experiments in the nonflaming mode, it seems that none of these products generate a quantity of any smoke component that is significantly more toxic to the rat than is the quantity of carbon monoxide produced. Therefore, it is unlikely that any bleed-air contaminant originating from lubricant decomposition in the engine will be more toxic than the CO content--which, in the Garrett/NTSB tests, was reported to be insignificant.

REFERENCES

- 1. San Francisco Examiner, Sunday, June 14, 1981.
- 2. <u>Oklahoma City Times</u>, "Fumes from Engine Cause Plane Crashes?", Monday, June 15, 1981.
- 3. Wizniak, E. P.: Special Investigation--An Evaluation of the Potential for Turbine Oil Byproduct Contamination of an Aircraft Cabin Environmental System. National Transportation Safety Board (publication pending, 1983).
- Crane, C. R., D. C. Sanders, B. R. Endecott, J. K. Abbott, and P. W. Smith: Inhalation Toxicology: I. Design of a Small-Animal Test System, II. Determination of the Relative Toxic Hazards of 75 Aircraft Cabin Materials. Federal Aviation Administration Report No. FAA-AM-77-9, 1977.
- Crane, C. R., D. C. Sanders, B. R. Endecott, J. K. Abbott: Electrical Insulation Fire Characteristics, Vol. II, Toxicity. Urban Mass Transportation Administration Report No. UMTA-MA-06-0025-79, II, 1978.