Reprinted from AEROSPACE MEDICINE, Volume 33, Pages 311-318, March, 1962

Presence of Ozone in Aircraft Flying at 35,000 Feet

W. A. YOUNG, M.D., D. B. SHAW, M.D. and D. V. BATES, M.D.

FOR MANY YEARS, it has been known that a layer of high ozone concentration is present in the lower stratosphere. Götz[9] states that practically the whole amount of atmospheric ozone exists between the altitudes of 10 and 50 kilometers. He describes a high primary layer of maximum ozone content at altitudes of 20 to 25 kilometers, and a secondary layer around 15 kilometers, which often merges with the higher layer. There is considerable latitudinal, local, seasonal, and diurnal variation. Several authors[3,4,8] have called attention to the probability that modern jet airliners are traveling at altitudes where they might be beginning to encounter appreciable ozone concentrations. They have also drawn attention to the fact that, if ozone is not destroyed in the compressors of the aircraft, still higher concentrations may exist in the crew and passenger compartments of these aircraft. While present-day aircraft are just flying in the lower boundary of the ozone layer, it appears likely that the next generation of aircraft may be operating in the middle of it.

The toxic effects of ozone on animals have been described in many papers for well over a century and recently Thorp[2] and Stokinger[17] have written comprehensive reviews of this subject. Stokinger[18] and Mittler, Hedrick, King and Gaynor[13] found the LC-50 for small animals to range from approximately four to thirty parts per million by volume,* the animals dying of pulmonary edema and hemorrhage. Instances of acute poisoning in humans have been rare, but Kleinfeld and Giel[11] and Kleinfeld, Giel and Tabershaw[12] have described three carefully-studied cases attributable to argon-shielded electric arc welding. These patients suffered severe and prolonged pneumonic illnesses from which they made eventual clinical recoveries. However, no measurements of pulmonary function were reported. The atmosphere in which they worked was found to contain concentrations of about 9 ppm of ozone. Truche[22] has also described a number of clinical cases but the possibility of the presence of oxides of nitrogen, which are also acute lung irritants, cannot be excluded.

A few studies of repeated exposures of animals to concentrations of the order of 1 to 10 ppm have been reported.[14,15,16,19] The pathological changes in the lungs consist of hyperplasia and sloughing of the bronchial epithelium, bronchiolar infiltrations and fibrosis sometimes extending into adjacent alveolar walls, and, occasionally, a mild degree of emphysema.[19] Few studies of the effects of low concentrations on humans have been done. However, Griswold, Chambers and Motley[10] describe a two-hour exposure to 2 ppm which produced an appreciable lowering of the vital capacity and timed vital capacity, the latter failing to return to normal at the end of 22 hours. Clamann and Bancroft[5] studied five subjects in concentrations of 1.2 to 6 ppm for varying periods of time

From the Cardio-Respiratory Service, McGill University Clinic, Royal Victoria Hospital, Montreal 2, Quebec.

The research for this paper was supported by the Defence Research Board of Canada, Grant Number 9310-84.

*"Parts per million by volume" has become the unit of ozone concentration most commonly used in physiological studies. It is obviously an extremely poor unit for expressing the amount of ozone present at different altitudes and different barometric pressures. In the opinion of the authors, it should be replaced by some unit related to the molecular concentration of ozone, such as partial pressure, moles per unit volume, or weight per unit volume. Throughout this paper, references to a concentration in "parts per million" or (ppm) mean: "equivalent to that concentration in parts per million by volume at sea level."

and demonstrated a fall in the carbon monoxide diffusing capacity of the lung.

The determination of ozone in air has been the subject of an extensive review by Thorp.[20]

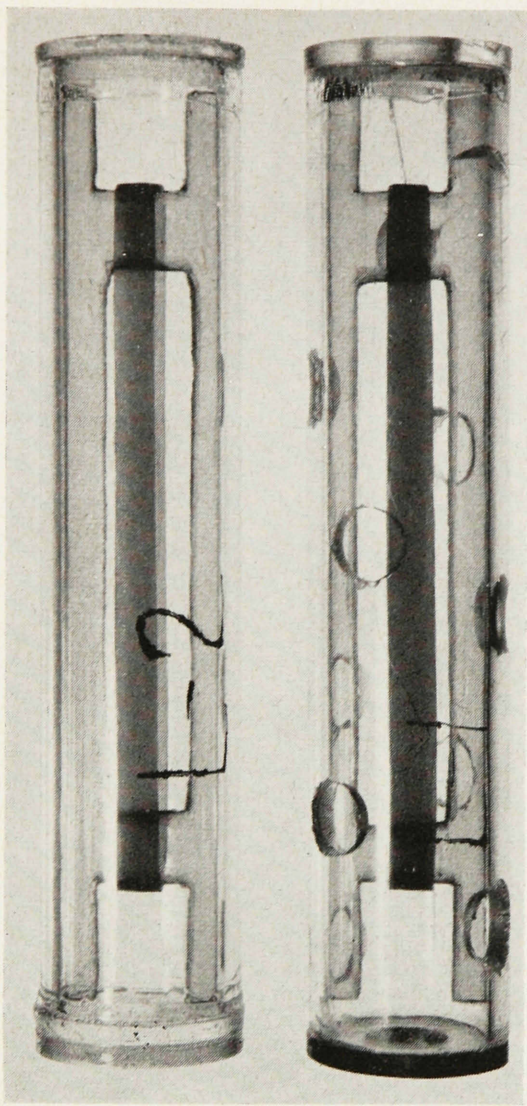

Fig. 1. Rubber bands on stretchers in sealed and open plastic tubes (15.5 x 3.2 cm.). Identical pairs were used throughout this study.

The most accurate method involves the use of an ultraviolet spectrophotometer. Chemical methods have centered chiefly around the oxidation of potassium iodide by ozone. This involves the use of liquids which would freeze at the low temperatures existing at the altitudes flown by jet aircraft and there is some disagreement as to the details of the method, chiefly with reference to the pH of the buffering system. Crabtree and Kemp[6] have studied in considerable detail the effect of ozone on stretched, natural rubber, and this has been used as the basis of a number of qualitative and semi-quantitative tests.[2,7] Although the test is somewhat crude, it appears to be quite specific, and possesses the advantage of simplicity.

METHODS

The Dominion Rubber Company Limited of Montreal prepared a batch of natural rubber containing a small amount of antioxidant. It was supplied in the form of bands approximately 8 x 0.8 x 0.16 cm. which were stretched on plastic frames to a length of 10.5 cm. (131 per cent of their original length). The frames were then placed in cylindrical plastic tubes (15 x 3 cm.) (Fig. 1), one of which was sealed, while the other contained holes in the top and sides to allow free passage of air. In all studies, one open and one sealed tube were placed side by side in the same location so that the sealed tube provided a control subjected to the same conditions of temperature and light as the open tube but not to the same variations of pressure or composition of the atmosphere.

One such pair of tubes was placed in each of the three following locations in three DC-8 aircraft:

1. Nosewheel well (unpressurized).
2. Crew compartment (pressurized).
3. Passenger compartment (pressurized).

An identical pair of bands was kept in the laboratory for comparison. The regular route of each aircraft was from Montreal to Vancouver and return, then to London, England, and return. The tubes were in place during August and September of 1960. They were removed for study after approximately six weeks flying, which added up to 325$\pm$15 hours of flying at altitudes of 27,000 to 39,000 feet (Fig. 2). Times below 27,000 feet were short and unlikely to involve appreciable exposure to ozone.

The following methods were used to assess the damage to the rubber bands:

1. *Visual Grading of Degree of Cracking.*—For this purpose, the following standards were used:

Grade 4: Gross, coarse fissures extending through more than 50 per cent of the thickness of the band and involving more than 80 per cent of the surface as seen with the naked eye.

Grade 3: Fine fissures (which may be very profuse) extending 25 per cent to 50 per cent through the thickness of the band and involving more than 80 per cent of the band's surface as seen with a low-power hand lens.

Grade 2: Very superficial fissuring extending less than 25 per cent of the thickness of the band and involving less than 80 per cent of the surface when viewed with a hand lens.

Grade 1: Bleaching and cracking visible but less than Grade 2.

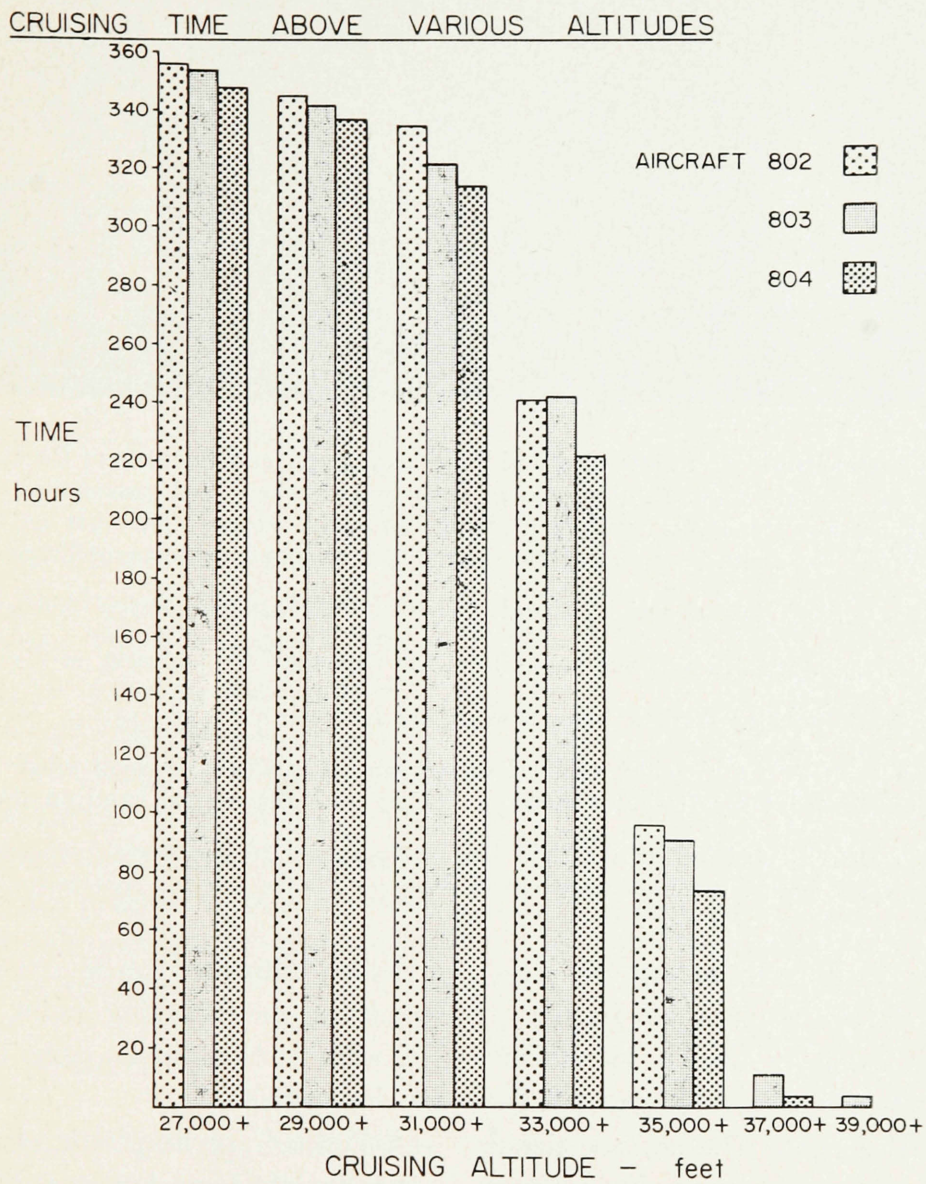

Fig. 2. Block graph of altitudes flown by the three aircraft. The columns represent the total time spent by the aircraft both at and above the altitudes shown.

Grade 0: Indistinguishable from a control band kept sealed in the laboratory.

2. *Modulus of Elasticity.*—This is the force per unit of cross-sectional area required to stretch a sample of material by its own length. Due to the fact that rubber is truly elastic over only a very small range of stretch, all measure-

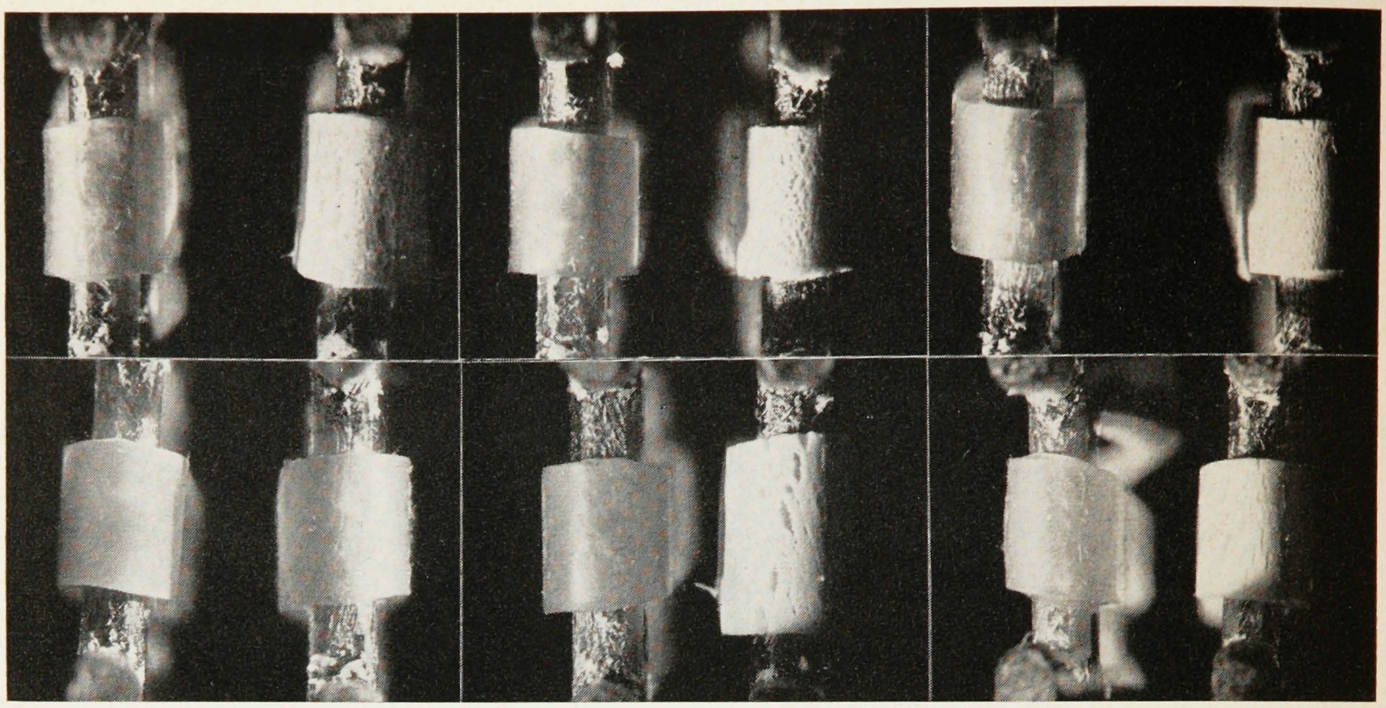

Fig. 3. *(Upper left)* Bands are from sealed and perforated (test) containers from the nosewheel well (unpressurized) of Aircraft No. 804. The end of each band is seen as it passes over the stretcher. That on the right shows the typical surface cracking caused by ozone, while that on the left is its undamaged control. The same arrangement has been followed in all subsequent illustrations.

Fig. 4. *(Upper center)* Sealed and test bands from the crew compartment of Aircraft No. 804.

Fig. 5. *(Upper right)* Sealed and test bands from the passenger compartment of Aircraft No. 804.

Fig. 6. *(Lower left)* Sealed and test bands kept in the laboratory.

Fig. 7. *(Lower center)* The bleached, cracked surface of the band on the right which has been exposed to 2.0 ppm of ozone for 51 hours contrasts sharply with the normal band on the left.

Fig. 8. *(Lower right)* The band on the right has been exposed to an average concentration of 0.5 ppm of ozone for 312 hours. An undamaged band is shown on the left for comparison.

ments were made from zero to ten per cent elongation. The force required to stretch a sample of rubber band by known increments was measured by means of a calibrated tension spring and two dial gauges. The cross-sectional area of the rubber band was measured at three points and a mean value taken for use in calculations. The force per unit area of cross-section was plotted against elongation and the modulus calculated from the straight-line part of the resulting graph. The results are expressed as dynes per square centimeter.

3. *"1300 Gram Stretch."*—This unorthodox test consisted in measuring the elongation of a three-centimeter section of the band by a 1300-gram weight.

Other suggested measurements of this type including ultimate tensile strength, increase in length at the breaking point, and permanent set, were carried out on some bands but proved too insensitive.

A 70-liter acrylic plastic chamber containing a small circulating fan was built for exposing rubber bands to ozone. Ozone was produced by ultra-violet irradiation of a stream of filtered, dried air by a small mercury vapor lamp (GE Ozone lamp—G 4S11), diluted by another stream of filtered dried air, and passed through the exposure chamber. Known concentrations of ozone were maintained in the chamber by adjusting the degree of dilution. The concentration of ozone in the chamber effluent was monitored continuously by a spectrophotometer measuring the absorption of ultra-violet light of wave-length 253.7 millimicrons (Ozone Analy-

TABLE I. BANDS CARRIED IN AIRCRAFT.

The Visual Grading of Damage goes from 0 (no damage) to 4 (most severe damage). The "Modulus of Elasticity" and "1300 Gram Stretch" for each exposed band have been expressed both in absolute units and as a percent of the values for the sealed control which accompanied it. The greater the damage to the band the weaker it becomes. Therefore, its "Modulus of Elasticity" becomes smaller, while its "1300 Gram Stretch" becomes greater. The term: "Laboratory Control" refers to the open and sealed bands kept in the laboratory while the other bands were in the aircraft.

O_3 EXPOSURE CONDITIONS	VISUAL GRADING OF DAMAGE	MODULUS OF ELASTICITY		1300 GM "STRETCH"	
		dynes/cm^2	% OF CONTROL	cms	% OF CONTROL
LABORATORY CONTROL	0	14.0×10^3		12·6	
2·0 ppm x 51 hrs	4	7·8 "	56	15·5	111
0·4 - 0·6 ppm x 312 hrs	4	6·5 "	47	17·2	123

ser, Beckman Model 52). This instrument has built-in standards based on physical interference with the light beam. The instrument readings were recorded by a printing, continuous-line recording milliammeter (Rustrak Model A).

Rubber bands in containers identical with those used in the aircraft were placed in the chamber and exposed to selected concentrations of ozone for varying periods of time in order to produce measurable damage for comparison with bands from the aircraft.

RESULTS

Figures 3, 4 and 5 show the bands from aircraft No. 804. The comparable bands from each of the other two aircraft showed an almost identical degree of cracking. It can be seen that the most severe damage has occurred in the band from the nosewheel well (unpressurized). The band from the crew compartment is somewhat less affected, and that from the passenger compartment least of the three. The cracking was usually more conspicuous at the ends of the band where it passed over the stretcher, but it involved the remainder in a similar, though often patchy, manner. Figure 6 shows a pair of bands kept at ground level while the other bands were in the aircraft. No cracking can be seen in these bands.

Table I summarizes the results on these bands. In most cases, the physical measurements (Modulus of Elasticity and "1300 Gram Stretch") support the visual grading of damage. Where there is disagreement, the latter is probably more reliable for two reasons: (1) the action of ozone on rubber is a surface phenomenon; (2) as the damage was often somewhat patchy, areas of fairly normal rubber might be present in the section of band which was tested. The open and sealed bands of the laboratory control pair showed no visible damage. The slight differences in the physical measurements of these two bands are insignificant.

In order to estimate the concentration of ozone required to reproduce the damage found in the bands from the aircraft, we exposed bands in the chamber to known concentrations of ozone, continuously for various periods of time. It was found that Grade 4 damage could be produced by 2.0 ppm for about 50 hours (Fig. 7), and by an average concentration of 0.5 ppm for about 300 hours (Fig. 8).

In the case of the latter band, the details of exposure were as follows:

	0.2 to 0.4 ppm	25 hours
	0.4 to 0.6 ppm	270 hours
	0.6 to 0.8 ppm	17 hours
Total	0.5 ± 0.3 ppm	312 hours

Table II summarizes the data on the bands shown in Figures 7 and 8. In each case, the modulus of elasticity agrees with the visual grading of damage but the "1300 Gram Stretch" shows less change than one would predict.

DISCUSSION

These results indicate that appreciable concentrations of ozone exist both inside and outside present day jet airliners. The changes in the bands indicate that the interior of the aircraft contains average concentrations of ozone a little below 0.5 ppm. The concentrations in the passenger compartments appear to be slightly less than that in the crew compartments. We would estimate these concentrations at 0.3 and 0.4 ppm, respectively.

The bands which had flown in the unpressurized, unheated nosewheel wells of the aircraft for approximately 325 hours, show a degree of damage almost identical with that produced in the laboratory by 0.5 ppm for about the same length of time. However, Crabtree and Kemp[6] found that a given concentration of ozone at very low temperatures produces fewer, but deeper cracks than at warmer temperatures. For this reason the bands from the nosewheel wells, which have been exposed to temperatures of the order −55° C, may not be exactly comparable with those exposed in the laboratory at room temperature. This objection, of course, does not apply to the comparison with the bands from the interior of the aircraft.

Nevertheless, it is of considerable interest that the concentrations of ozone inside the aircraft are almost certainly no higher, and probably a little lower than outside. The reverse would be expected if no ozone were destroyed by heat during compression of the air to cabin conditions. It is known that the temperature reaches at least 200° F during the process of compression, but the time of exposure is very short. On the other hand, the possibility cannot be excluded that some ozone may be manufactured within the aircraft by the large amount of electrical equipment in operation.

In any case, it appears that the average concentration of ozone in the cabin of these aircraft during flight is several times the maximum permissible limit of 0.1 ppm recommended by the American Conference of Governmental Industrial Hygienists.[1] Our results do not indicate

TABLE II. BANDS EXPOSED TO KNOWN OZONE CONCENTRATIONS.
Data on two bands exposed to ozone in the laboratory (Figs. 7 and 8) are compared with a single unexposed control band.

AIRCRAFT	LOCATION	C= CONTROL E= EXPOSED	VISUAL GRADING OF DAMAGE	MODULUS OF ELASTICITY dynes/cm²	% of CONTROL	1300 GM "STRETCH" cms	% of CONTROL
	LABORATORY CONTROL	C	0	14·0 x 10³		12·6	
		E	0	13·3 "	95	11·5	91
802	NOSEWHEEL WELL	C	0	11·3 "		10·8	
		E	4	6·9 "	61	16·6	154
802	CREW COMPARTMENT	C	0	12·0 "		10·6	
		E	4	7·6 "	63	15·9	150
802	PASSENGER CABIN	C	0	12·2 "		10·7	
		E	3	12·0 "	98	11·9	111
803	NOSEWHEEL WELL	C	0	13·3 "		10·7	
		E	4	6·1 "	46	16·5	154
803	CREW COMPARTMENT	C	0	13·1 "		11·2	
		E	3	11·9 "	91	15·2	136
803	PASSENGER CABIN	C	0	13·4 "		13·2	
		E	2	11·5 "	86	13·2	100
804	NOSEWHEEL WELL	C	0	12 8 "		12·7	
		E	4	7 2 "	56	17·0	134
804	CREW COMPARTMENT	C	0	12 7 "		12·9	
		E	3	10 5 "	83	14·8	115
804	PASSENGER CABIN	C	0	13 7 "		10·1	
		E	2	11 4 "	83	10·6	105

whether this is a constant concentration or an intermittent one due to occasional passage through areas of high ozone content, but the latter possibility seems more likely. These concentrations present no hazard to passengers, who would usually have infrequent exposures of a few hours duration. The possibility of pulmonary damage to crew members remains unknown but deserves careful study. It should be noted however that the limits advised by the American Conference of Governmental Industrial Hygienists apply to workers exposed for 40 hours per week which is about twice the usual exposure-time of aircrew.

In this regard, Kleinfeld, Giel and Tabershaw[12] reported frequent upper respiratory tract irritation in welders from a plant where the ozone concentration ranged from 0.3 to 0.8 ppm and no symptoms in welders from a plant with an atmosphere containing 0.25 ppm. However, no measurements of pulmonary function were made. We recently examined seven welders from a plant whose atmosphere contained between 0.2 and 0.3 ppm of ozone.[23] Only one complained of irritation of conjunctivae and upper respiratory tract. Chest radiographs of all seven showed no abnormalities. Vital capacity was below the predicted value in two, but expiratory flow rates and carbon monoxide diffusing capacities were normal in all cases.

SUMMARY

The presence of ozone in DC-8 jet aircraft flying between 27,000 and 39,000 feet was detected by its property of cracking stretched natural rubber. Similar rubber bands were exposed to known concentrations of ozone for set periods of time. By comparing these bands with those from the aircraft, it was estimated that the average concentration of ozone inside the aircraft is about 0.3 to 0.4 ppm and is slightly higher in the crew compartment than in the passenger cabin. The concentration outside the aircraft is probably equivalent to about 0.5 ppm at sea level. Although the compressed atmosphere of the interior of the aircraft does not contain more ozone than the rarefied outside atmosphere, the concentrations detected are nevertheless several times greater than the upper limits permitted in industry.[1] It is expected that the concentrations will be even higher in future aircraft which will be flying well within the ozone-layer, unless precautionary measures are taken.

ADDENDUM

Since the completion of this experiment, a "Viscount" turbo-prop and a "Super-Constellation" piston-engine aircraft, as well as another DC-8, have been tested for the presence of ozone. The concentrations in the DC-8 were identical with those described above. The other two aircraft which cruised at altitudes of 11,000 to 23,000 feet contained only minute traces of ozone. This confirms our belief that the ozone found in the aircraft at the higher altitudes comes from the outside atmosphere and is not generated by the electrical equipment within the aircraft.

ACKNOWLEDGMENTS

This work was financed by Grant Number 9310-84 from the Defence Research Board of Canada. It was made possible only by the active co-operation of Mr. J. T. Dyment, Chief Engineer of Trans-Canada Airlines, and his staff, to whom we are greatly indebted. We also wish to thank the technical staff of the Dominion Rubber Company in Montreal, for making the rubber bands used throughout these studies.

REFERENCES

1. American Conference of Governmental Industrial Hygienists, Threshold Limit Values for 1960. *Arch. Environ. Health*, 1:140, 1960.
2. Beatty, J. R. and Jave, A. E.: A simple objective method for estimating low concentrations of ozone in air. *Rubber Chem. Techn.*, 28:608, 1955.
3. Bowen, I. G.: The measurement of atmospheric ozone. *In* Aviation Medicine-Selected Reviews, pp. 39-44. Pergamon Press: 1958.
4. Clamman, H. G. and Bancroft, R. W.: Physiological effects of ozone. *Fed. Proc.*, 16:22, 1957.
5. Clamman, H. G. and Bancroft, R. W.: Toxicity of ozone in high altitude flight. *In* Ozone Chemistry and Technology, pp. 352-359. *American Chemical Society*, 1959.

6. CRABTREE, J. and KEMP, A. R.: Weathering of soft vulcanized rubber. *Industr. Eng. Chem.*, 38:278, 1946.
7. CRABTREE, J. and KEMP, A. R.: Accelerated ozone weathering test for rubber. *Industr. Eng. Chem.* (Analytical Edition), 18:769, 1946.
8. ERNSTING, J.: Physiologic aspects of the significance of ozone in pressurized cabins. I.A.M. Memorandum No. S-20 (R.A.F. Farnborough) September, 1959.
9. GÖTZ, F. W. P.: Compendium of meteorology. Boston: American Meteorological Society, 1951.
10. GRISWOLD, S. S., CHAMBERS, L. A., and MOTLEY, H. L.: Report of a case of exposure to high ozone concentrations for two hours. *AMA Arch. Industr. Health*, 15:108, 1957.
11. KLEINFELD, M. and GIEL, C. P.: Clinical manifestations of ozone poisoning (report of a new source of exposure). *Amer. J. Med. Sci.*, 231:638, 1956.
12. KLEINFELD, M., GIEL, C. P. and TABERSHAW, R.: Health Hazards associated with inert gas-shielded metal arc welding. *AMA Arch. Industr. Health*, 15:27, 1957.
13. MITTLER, S., HEDRICK, D., KING, M. and GAYNOR, A.: Toxicity of ozone: I Acute toxicity. *Industr. Med. Surg.*, 25:301, 1956.
14. MITTLER, S., KING, M. and BURKHARDT, B.: Toxicity of ozone: III Chronic toxicity. *AMA Arch. Industr. Health*, 15:191, 1957.
15. SCHEEL, L. D., DOBROGORSKI, O. J., MOUNTAIN, J. T., SVIRBELY, J. L. and STOKINGER, H. E.: Physiological, biochemical, immunological and pathological changes following ozone exposure. *J. Appl. Physiol.*, 14:67, 1959.
16. SCHULZ, H.: Chronic ozone poisoning. *Arch. Exp. Pathol. Pharmakol.*, 29:364, 1892.
17. STOKINGER, H. E.: Ozone toxicity: A review of the literature through 1953. *AMA Arch. Industr. Hyg. & Occ. Med.*, 9:366, 1954.
18. STOKINGER, H. E.: Evaluation of the hazards of ozone and oxides of nitrogen: Factors modifying toxicity. *AMA Arch. Industr. Health*, 15:181, 1957.
19. STOKINGER, H. E., WAGNER, W. D., DOBROGORSKI, O. J.: Ozone toxicity studies: III Chronic injury to lungs of animals following exposure at low level. *AMA Arch. Industr. Health*, 16:514, 1957.
20. THORP, C. E.: Bibliography of Ozone Technology. Vol. I. Chicago: Armour Research Foundation, Illinois Institute of Technology, 1954.
21. THORP, C. E.: Bibliography of Ozone Technology. Vol. II. Chicago: Armour Research Foundation, Illinois Institute of Technology, 1955.
22. TRUCHE, R.: Toxicity of ozone. *Arch. Mal. Prof.*, 12:55, 1951.
23. YOUNG, W. A. and SHAW, D. B.: Unpublished data.

Printed in USA