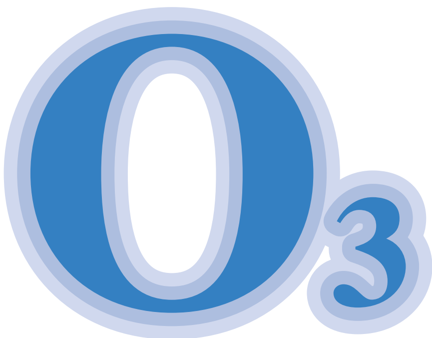
P-E00-6A

Ozone Resistant Pneumatic Equipment

(The use of pneumatic equipment in low ozone concentration environments)



SMC CORPORATION

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1. Pneumatic Equipment Malfunctions Caused by Ozone

• Types of Malfunctions Caused by Ozone

Ozone can cause rubber materials (mostly NBR) used in pneumatic equipment to crack, and thereby lead to air leakage and malfunction.

Types of damage and malfunctions

Devices	Damaged parts	Results
Regulator	Diaphragm Photo 1	• Constant air leakage from bleed hole • Unable to adjust pressure
	Main valve seat	• Constant air leakage from bleed hole • Unable to adjust pressure
Speed control valve	Valve seat rubber for check valve Check valve seal Photo 2	• Unable to adjust pressure
Solenoid valve	Main valve seal Photo 3	• Air leakage, Malfunction
	Gasket	• Air leakage, Malfunction
Cylinder (Actuator)	Seals are coated with a lubricant that has a shielding effect from ozone. Damage does not occur. For cylinders lubricated by a compressed air system lubricator, the oil film that is provided to components in this way is equivalent to a grease coat in its protective effects. Even with non-lube type cylinders, grease protects seals from being damaged. (Refer to Grease Coat Protection Effect on page 4.)	

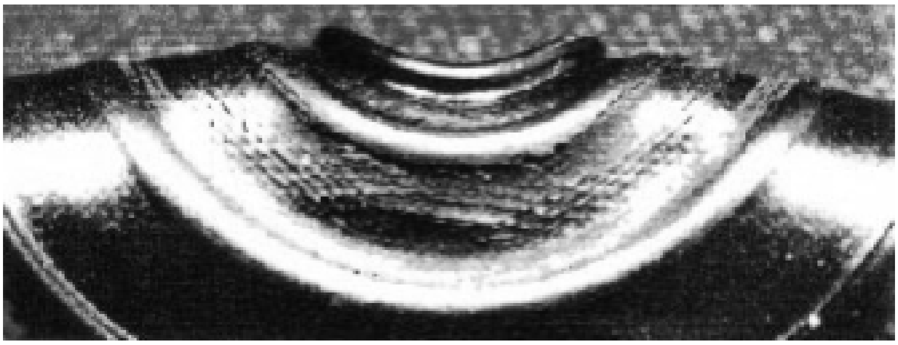


Photo 1 Cracking of diaphragm

Photo 2 Cracking of check valve seal

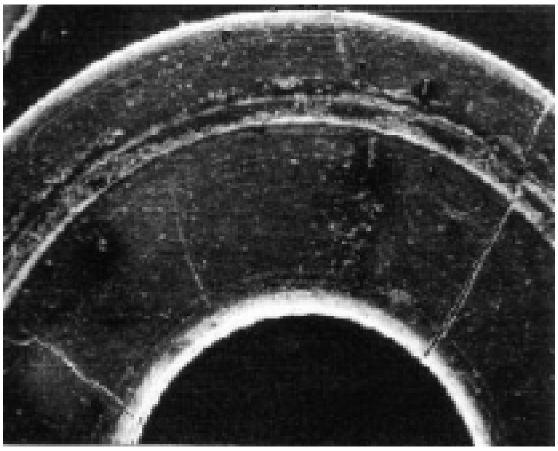


Photo 3 Cracking of main valve seal

• Ozone Concentration and the Time It Takes for Ozone to Generate Cracks (Deterioration) on Rubber

In most cases, there is a clear-cut relationship between ozone concentration (C) and the time it takes for ozone to generate cracks (τ)*.

$$\tau \cdot C^n = \text{Const.}$$

τ: Time it takes for ozone to generate cracks (h)
C: Ozone concentration (ppm)
n: Constant that varies depending on the rubber material

Take the logarithm and rearrange the above equation as follows:

$$\log\tau = K - n \log C$$

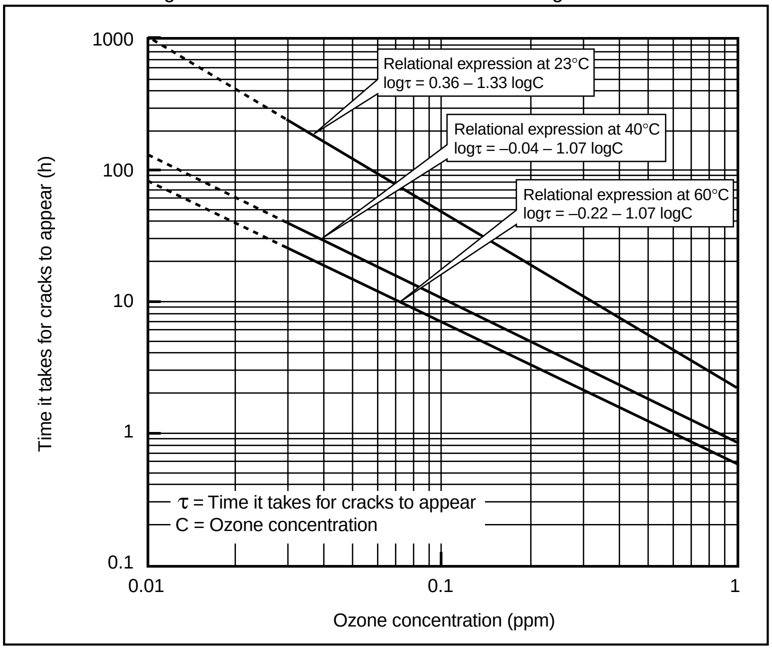
K: Constant

* YU.S Zuev and S.I. Pravednikova "Rubber Chemistry and Technology" (1962) Page 411 to 420

Linear relationships were obtained when plotting the logarithms of the experiments SMC conducted on ozone concentration and the time it takes for ozone to generate cracks. What became evident is that as ozone concentration increases, the time it takes for ozone to generate cracks decreases. These tests were conducted under conditions that are much more severe than those of a normal operating environment, and were likewise evaluated more stringently. The solid lines in the graph indicate actual measurements gathered during the tests, and the dotted lines are estimated values obtained from calculations. Changes in ozone concentration greatly affect the time it takes for ozone to generate cracks.

Ozone concentration and its direct relation to the appearance of cracks (time factor) (NBR)

JIS K6259: Testing Methods of Resistance to Ozone Cracking for Vulcanized Rubber



<Test conditions>
Specimen: I-shaped dumbbell
Tensile strain: 20 ±2%
Evaluation: Cracking detection using a magnified 50x metallurgical microscope

• Basic Structure and Ozone Resistance

Molecular structure

Ozone resistance of NBR and HNBR varies depending on its structure.

Basic molecular structures

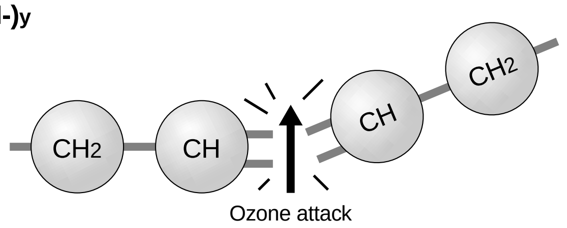
Rubber type	Basic molecular structure
NBR (acrylonitrile-butadiene rubber)	$(\text{-CH}_2\text{-CH=CH-CH}_2\text{-})_x \text{ — } (\text{-CH}_2\text{-CH(CN)-})_y$
HNBR (hydrogenated nitrile butadiene rubber)	$(\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-})_x \text{ — } (\text{-CH}_2\text{-CH(CN)-})_y$

Double bond

Deterioration caused by ozone occurs when ozone acts on the NBR double bond to break the rubber molecules apart.

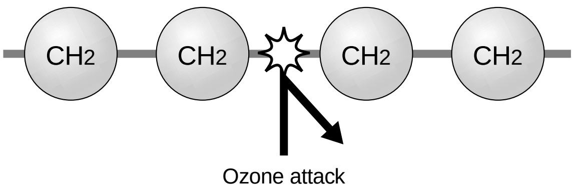
$$\text{NBR } (\text{-CH}_2\text{-}\underline{\text{CH=CH}}\text{-CH}_2\text{-})_x \text{ — } (\text{-CH}_2\text{-}\underset{\text{CN}}{\underset{|}{\text{CH}}}\text{-})_y$$

Double bond



On the other hand, HNBR's basic structure, which is becoming more and more standard, eliminates the double bond of NBR by adding hydrogen. Although a minute amount of double bond remains in the structure of HNBR to allow it to maintain its physicality as a rubber, its structure has an excellent ozone resistance.

$$\text{HNBR } (\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-})_x \text{ — } (\text{-CH}_2\text{-}\underset{\text{CN}}{\underset{|}{\text{CH}}}\text{-})_y$$



Ozone resistance

An experiment was performed under test conditions conforming to JIS K6259, and using air containing 1ppm of ozone. The test conditions (ozone concentration, temperature, and tensile strain) were much more severe than those in a normal operating environment; therefore, cracks were evident in NBR in just 1 to 25 hours of exposure to ozonic air. On the other hand, when the same stringent conditions were applied to HNBR, cracks did not appear even after 1000 hours of exposure.

Ozone resistance

Rubber type	Time it takes for ozone to generate cracks
NBR	1 to 25hrs.
HNBR	1000hrs. or more

<Test conditions>
Ozone concentration: 1ppm
Specimen: I-shaped dumbbell
Tensile strain: 20 ±2%
Testing temperature: 40 ±1°C

• Grease Coat Protection Effect

A coating of grease or other lubricants is an effective way to shield NBR parts from ozone attack. When the protective effects of grease were tested and measured, it was found that cracks began to appear after 1 to 25 hours of ozone exposure on NBR components that had not been given a grease coating. On the other hand, cracks did not appear on the components that had received a grease coating, even after more than 1000 hours of ozone exposure. The reasons given for these results are the physical shielding effects of grease, as well as its chemical effects as it reacts to ozone and accelerates its decomposition.
Therefore, no ozone generated cracks were found on components whose seals or seal surfaces are normally treated with a coat of grease (lubricant), e.g., cylinders, rotary actuators, or quick disconnect release couplings (One-touch fittings).

Grease coat protection effect
JIS K6259: Testing Methods of Resistance to Ozone Cracking for Vulcanized Rubber

	Time it takes for ozone to generate cracks
Uncoated NBR	1 to 25hrs.
Grease coated NBR	1000hrs. or more

<Test conditions>
Ozone concentration: 1ppm
Specimen: I-shaped dumbbell
Tensile strain: 20 ±2%
Testing temperature: 40 ±1°C
Amount of grease applied: 6.3mg/cm²

3. The Deteriorating Effect of Ozone

• Causes and Progression of Deterioration due to Ozone

How ozone gets into a pneumatic system

From measurements taken to date, we know with certainty that the concentration of ozone in the air that a pneumatic system compressor takes in is at most 0.1ppm at a standard atmospheric pressure rating. Factory machinery and equipment are primary sources of ozone. Nevertheless, ozone can also be found in nature along with photochemical oxidants. (Refer to page 11 for details.)

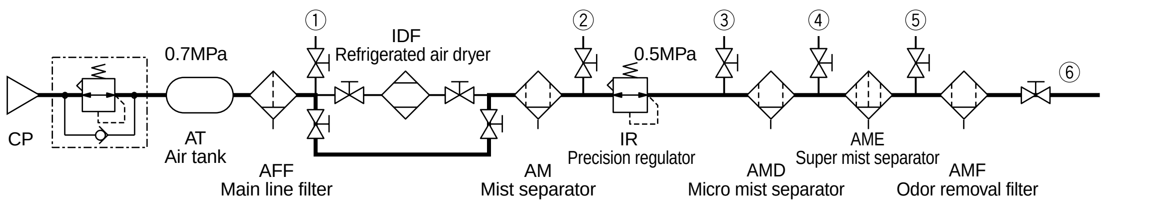
When compressed air containing ozone (possibly generated from other machinery and equipment present in a plant) enters a pneumatic system, it adversely affects the system's rubber components. Besides the more commonly recognized sources of ozone described under "Ozone Emitting Equipment and Devices" on page 8, an air compressor motor that is not maintained and serviced at the proper scheduled intervals can also become a source of ozone emissions.

Traditionally, lube type reciprocating compressors have been widely used in pneumatic systems. Through the use of these ozone-efficient compressors, the amount of ozone in a pneumatic system could be reduced, and its effects in lines nullified, by the heat produced during compression and by the action of draining condensate out of the system. In recent years, however, the widespread use of non-lube type turbocompressors and displacement compressors (dry rotary type) has decreased the chances for ozone depletion in lines.

• Fluctuations to Ozone Concentration in Pneumatic Circuits

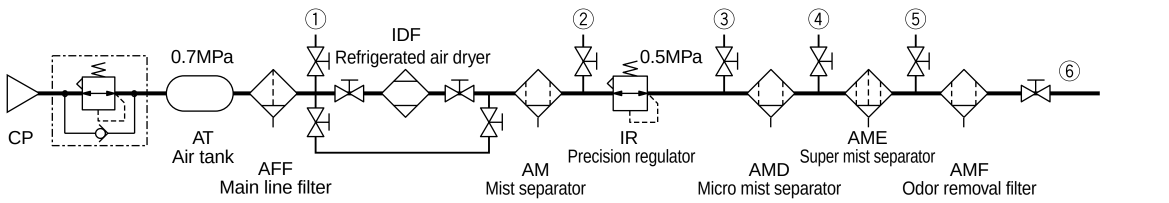
An ozonizer was used to prepare air with ozone concentration rates of 1.1ppm and 0.1ppm. The air was introduced into the lines in the system through the compressor's intake port, and measurements were taken of changes in the concentration of ozone after the air passed through the various filters, dryers, and regulators. Since it is extremely difficult to measure the ozone concentration in pressurized air while it is in lines, samplings of pressurized air were taken from certain points in the pneumatic circuit (see ① to ⑥ below) and the ozone concentration was measured immediately, using an ultraviolet absorbent densitometer (EG-2001F made by EBARA JITSUGYO CO., LTD).

Pneumatic circuitry at an atmospheric dew point of 10°C (Circuit not passing through refrigerated air dryer)



∗ The bold line is the testing circuit.

Pneumatic circuitry at an atmospheric dew point of –17°C (Circuit passing through refrigerated air dryer)



∗ The bold line is the testing circuit.

The residual ozone ratio in pneumatic lines

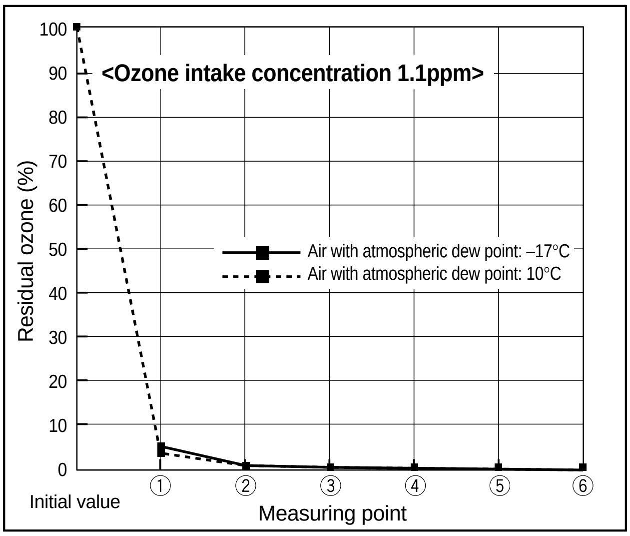
In the lines of lube-type reciprocating compressor, with intake air containing a concentration of 1.1ppm of ozone, the ozone is phased out as follows:

- Some 95% or more of the ozone is eliminated as air passes through the main line filter (AFF) — as measured at point ① which is just downstream of the AFF in the circuit.
- Most of the remainder is eliminated as air passes through the refrigerated air dryer (IDF) and mist separator (AM) — as measured at point ②, just downstream of these components in the circuit.

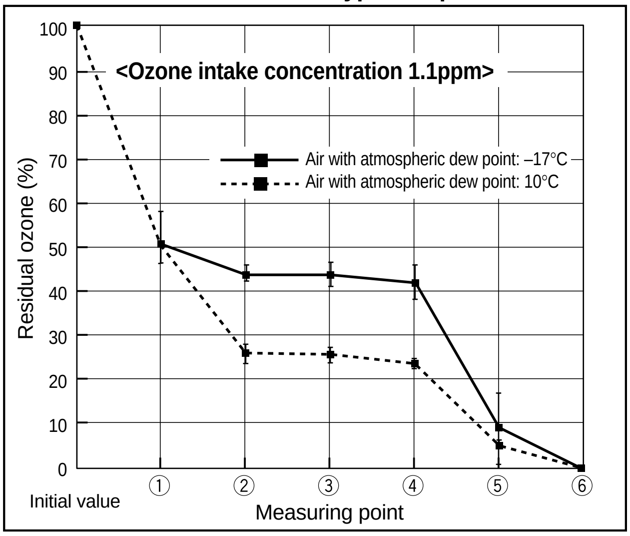
Ozone depletion is much slower in a non-lube scroll type compressor than in a lube type reciprocating compressor. At the same ozone concentration of 1.1ppm, approximately 25% of the ozone still remains in the circuit as measured at point ② — downstream of the mist separator (AM) — at an atmospheric dew point of 10°C. When the atmospheric dew point is –17°C, approximately 45% of the ozone still remains. Furthermore, with an ozone concentration as low as 0.1ppm in intake air, fast ozone depletion is evident just until after air passes through the main line filter (AFF) — as measured at point ① in the circuit. After that point, however, ozone depletion is as slow as if the concentration were greater — i.e., as if it were an original concentration of 1.1ppm. Even after the air has passed through the micromist separator (AMD), a very small residual quantity can still be found in lines at point ④, just downstream.

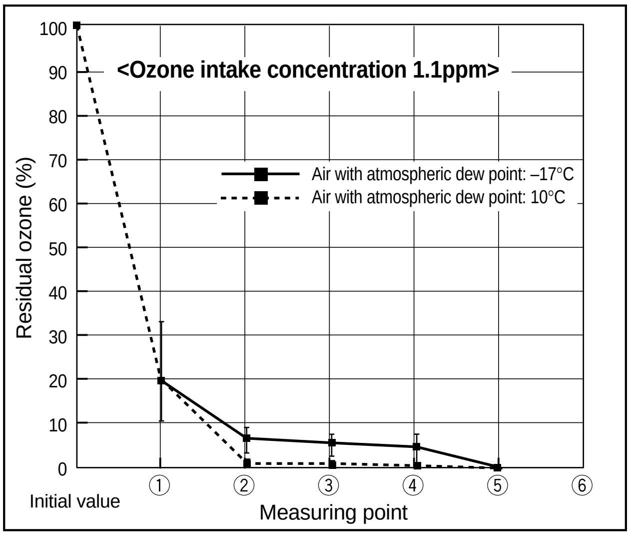
These observations illustrate that the use of so-called "oil-free" air sources and compressed air at low dew points make it difficult to eliminate ozone in pneumatic lines.

The residual ozone ratio in the lines of lube type reciprocating compressor



Changes in the residual ozone ratio in the lines of non-lube scroll type compressor





4. Ozone Resistance of Standard (HNBR) Products

• Setting

Even when ozone is present in compressed air, its concentration is depleted as it travels through the lines in a pneumatic circuit. (Refer to "Fluctuations in the Concentration of Ozone within a Pneumatic System" on page 5.) However, the ratio of ozone depletion, and the harm that residual ozone can cause to pneumatic circuitry, varies according to the equipment and components that are implemented in the particular pneumatic circuit. NBR, for example, is a material that can suffer deterioration caused by residual ozone.

Evaluation criteria for ozone resistance

SMC's evaluation criteria for ozone resistance in its products can be defined as follows:

Products meeting a 5-year (or 43,800 hours) resistance rating (or equivalent) under working conditions that include 40°C ambient and fluid temperatures and an ozone concentration of 0.03ppm in 0.5MPa compressed air. These standards assume the normal concentration of ozone usually found in the atmosphere, and the ozone depletion that takes place in a pneumatic circuit, but allow for wide tolerance margins in product design.

Please refer to the "List of Ozone Resistant Products 1: Standard (HNBR)" on page 9 to familiarize yourself with standard products using HNBR.

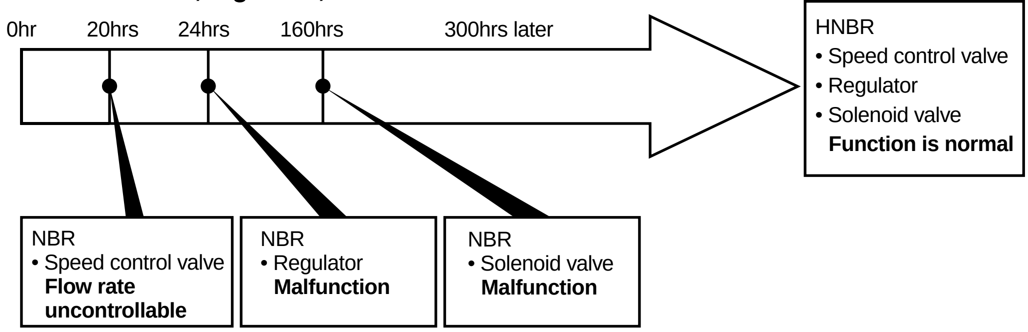
For non-HNBR devices that nevertheless afford superior ozone protection, please refer to the "List of Ozone Resistant Products 2: Series 80-" on page 10.

• Endurance Test

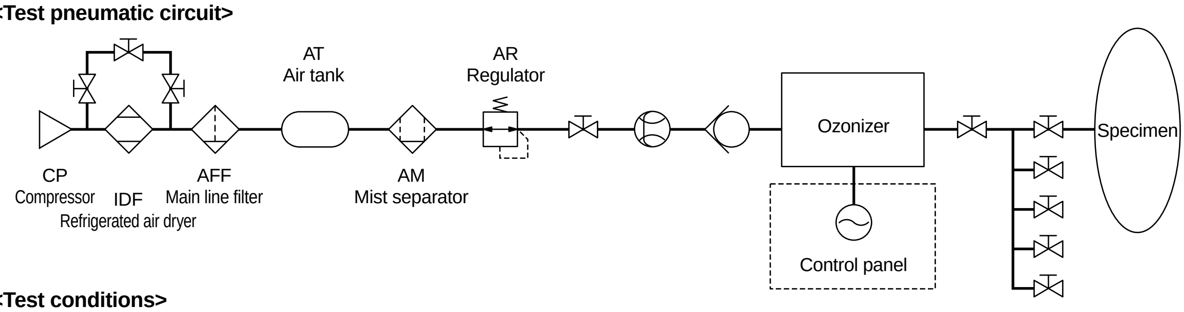
An ozonizer was used in a pneumatic circuit to prepare air to an ozone concentration of 1ppm. The test specimens (system components made from HNBR and NBR) were operated using this ozone-laden compressed air, and the endurance of each type of component/material was measured and compared.

Endurance test: Speed control valve, regulator, solenoid valve

<Endurance test results>



<Test pneumatic circuit>



<Test conditions>

Models			Ozone resistance evaluation	
			Conditions	Operating frequency
Speed control valve	Series AS-F AS1000, 1400 AS12□0 to AS42□0	NBR	Ozone concentration: 1ppm Inlet pressure: 0.7MPa Set pressure: 0.5MPa Ambient temperature: 23°C	ON 0.5 sec OFF 0.5 sec
		HNBR		
Regulator	AR1000 to 6000	NBR		
	AW1000 to 4000	HNBR		
Solenoid valve	VQ1201H-5	NBR		1Hz
		HNBR		

Line: Polyurethane tube (TU0604); Fitting: Quick disconnect release coupling (One-touch fitting KQ2)

5. Ozone

• What is Ozone?

Ozone is an allotrope of oxygen, and small quantities of it are present in air. It is formed by electrical discharges in dry gaseous oxygen or air. It is also formed through the heating of fluorine, water, oxygen, and through the exposure of air to ultraviolet irradiation or X-rays. A light-blue gas with a distinctive odor, it is highly oxidative and is used for sterilization, bleaching, and oxidation purposes.

Since ozone is highly poisonous, large concentrations of it can affect the respiratory system. Even a small quantity of this gas can be toxic if inhaled for long periods.

Normal concentration of ozone in the atmosphere is between 0 and 0.03ppm, but when ozone emissions from the "Ozone Emitting Equipment and Devices" table below are added to the normal atmospheric level, the concentration could reach up to 0.1ppm.

• Ozone Exposure Concentration and Its Physical Effects

Ozone (ppm)	Effects
0.01 to 0.02	Odor is somewhat detectable by smell (but after a while, it becomes indistinguishable).
0.1	Odor is clearly detectable by smell. Nose and throat can feel an irritating sensation.
0.2 to 0.6	Impairs vision after 3 to 6 hours of exposure
0.5	Definite irritating sensation can be felt in upper respiratory passage.
1 to 2	Headache, chest pain, dryness in upper respiratory passage, and coughing after 2 hours of exposure. Repeated exposure can cause chronic poisoning.

Reference: Hidetoshi Sugimitsu, *Ozone no Kiso to Oyo ("Basis and Application of Ozone")* Korin Co., Inc., (1996)

• Standard Ozone Concentration in Working Environments in Various Countries

Country	Ozone concentration (ppm)
Australia	0.1
Belgium	0.1*
Denmark	0.1
Finland	0.1
France	0.1
Germany	0.1

Country	Ozone concentration (ppm)
Japan	0.1
Sweden	0.1
Switzerland	0.1
Great Britain	0.1
United States	0.1*
Russia	0.1

TWA — Time Weighted Average: Level of ozone that is considered non-hazardous to almost all workers if the time average of ozone exposure concentration is below the indicated value. This condition applies when workers are engaged in physically light labor for 8 hours a day, 40 hours a week.

*STEL — Short Time Exposure Limit: Applied to toxic substances that mainly affect living organisms after short time exposure. For our purposes, it refers to a level of ozone that is considered non-hazardous to almost all workers if the time average value for 15 minutes is below the indicated value.

Reference: ILO OCCUPATIONAL SAFETY AND HEALTH SERIES NO. 37 (THIRD EDITION 1991)

• Ozone Emitting Equipment and Devices

Because ozone is easily formed by electric discharges or light energy, many ozone emitting devices may be found in the workplace or in the home.

Devices	Ozone formation	Ozone concentration	Environment
Air purifier	Corona discharge	A few ppm	Office environment, Household environment
Sterilizer	Ultraviolet light	A few ppm	Office environment, Household environment
Ultraviolet curing device	Ultraviolet light	A few dozen ppm	Industrial environment
Copy machine, Printer	Corona discharge	Up to a few dozen ppm	Office environment, Household environment
Welding machine	Ultraviolet rays, Arc discharge	A few ppm	Industrial environment
Static removal equipment	Electrical discharge	A few dozen ppm	Industrial environment, Office environment
Surface finishing machine	Electrical discharge, Ozonizer	More than a hundred and less than 100,000 ppm	Industrial environment
Electron beam, X-ray irradiation machine	Electron beam, X-rays	More than a hundred and less than 10,000 ppm	Industrial environment
High voltage electric generating plant	Electrical discharge	Up to a few dozen ppm	Industrial environment
Semiconductor dry cleaner	Ultraviolet light, Electrical discharge	More than a hundred and less than 100,000 ppm	Industrial environment
Electric dust collector	Corona discharge	A few ppm	Industrial environment

Reference: Shigeyuki Ota and Hironori Shimizu (Eds) *Ozone Riyo no Riron to Jissai ("Theory and Practice of Ozone Use")* Riaraizu Co., Inc., (1989)

List of Ozone Resistant Products 1: Standard (HNBR)

Description		Series	
Directional control valves	4-, 5-port solenoid valve	VQ	0000 1000 2000 4000 5000
		VQZ	1000 2000 3000
		SQ	1000 2000
		VQD	1000
		SY	3000 5000 7000
		SYJ	3000 5000 7000
		SX	3000 5000 7000
	3-port solenoid valve (2)	VQ	20, 30
		VQ	100
		VQZ	100 200 300
		SY	100 300 500
		SYJ	300 500 700
Pressure control valves	Regulator	AR	1000 2000 2500 3000 4000 4000-06 5000 6000
	Filter regulator	AW	1000 2000 3000 4000 4000-06
	Regulator with residual pressure exhaust	AR	2550 3050 4050 4050-06
	Filter regulator with residual pressure exhaust	AW	3050 4050 4050-06
	Regulator with reverse flow check valve	AR	2060 2560 3060 4060 4060-06 5060 6060
	Pressure regulator with internal pilot	AR	425 625 825 925
	Direct operated precision regulator	ARP	3000
	Miniature regulator	ARJ	210 1020
	MR Unit	AMR	3□00 4□00 5□00 6□00

Description		Series	
Pressure control valves	Manifold regulator	ARM	1000 2000 2500 3000
	Mist separator regulator	AWM	2000 3000 4000
	Micro mist separator regulator	AWD	2000 3000 4000
Flow control valves	Speed controller	AS	1000-M3 1200-M3 1400-M3 1000-M5 12□0-M3 (U10, 32) 12□0-M5-F 22□0-□01 22□0-01-F 22□0-□02 22□0-02-F 32□0-□03 (02) 32□0-03-F (02)
	Speed controller	AS	42□0-□04 42□0-04-F 12□1F□-M3 13□1F□-M3 12□1F□-M5 (U10, 32) 13□1F□-M5 (U10, 32) 22□1F□-□01 23□1F□-□01 2211F-01-06 22□1F□-□02 23□1F□-□02 32□1F□-□03 (02) 33□1F□-□03 (02) 42□1F-□04 43□1F-□04 1000F 2000F 2050F 3000F 4000F 1001F 2001F 2051F 3001F 4001F
		ASD	230F 330F 430F 530F 630F
		ASP	330F 430F 530F 630F
Vacuum products	Vacuum ejector	ZM ZZM	

SMC

List of Ozone Resistant Non-HNBR type Products 2: Series 80-

Description		Series	Note
Directional control valves	4, 5-port solenoid valve	80-VF3000 80-VF5000 80-VK3000	
	3-port solenoid valve	80-VP300 80-VP500 80-VP700 80-VJ100 80-VT307 80-VT317 80-VK300 80-VKF300	
	Mechanical valve	80-VM130-01-00 80-VM230-02-00 80-VM430-01-00 80-VZM450-01-00 80-VZM550-01-00 80-VFM350-02-00	
	3-port residual pressure release valve	80-VHS400 80-VHS500	
	3-port residual pressure release valve with keyhole	80-VHS2500 80-VHS3500 80-VHS4500	
	3-port residual pressure release valve	80-VHS2000 80-VHS3000 80-VHS4000	
Power valves	Regulator valve	80-VEX120☐- 80-VEX130☐- 80-VEX150☐- 80-VEX170☐-	Air operated type only
	Precision regulator valve	VEX1A33B VEX1B33B	Standard: Fluoro rubber
		80-VEX1233- 80-VEX1533- 80-VEX1733-	
	3-position valve	80-VEX350☐	Air operated type only
Pressure control valves	Pilot operated pressure regulator	80-AR435 to 935	
	Clean room regulator	SRH3000 SRH4000	
	Precision regulator valve	80-IR1000 80-IR2000 80-IR3000	
	Electro-pneumatic regulator	80-ITV0000 80-ITV1000 80-ITV2000	
	Electronic vacuum regulator	80-ITV209☐	
Flow conrol valves	Check valve	80-AK	
	Quick exhaust valve	80-AQ	
Vacuum products	Vacuum (ejector system)	80-ZX1☐	

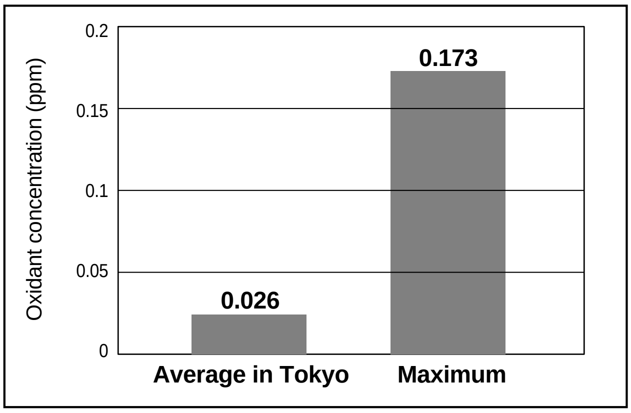
Reference Data

Photochemical Oxidants

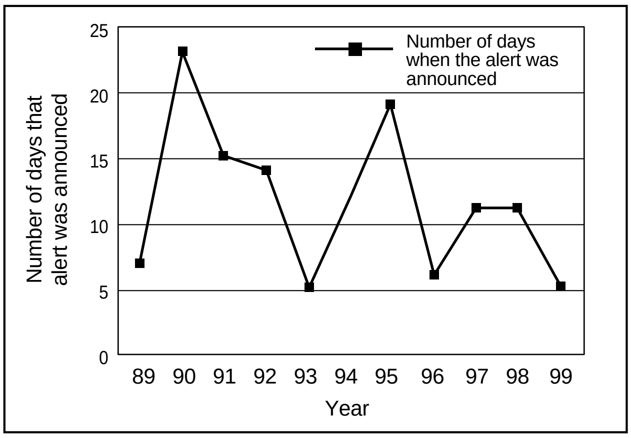
"Photochemical oxidants" is a general term used to refer to a type of secondary pollutants that in their original (primary state) are mainly composed of industrial and automobile emissions of nitrogen oxide (NO_X) and hydrocarbons (HC). When these contaminants are exposed to sunlight irradiation, they experience a photochemical reaction that changes their composition into photochemical oxidants. The adverse environmental effects of their altered secondary nature are equivalent to a 60 to 90% concentration of ozone.

According to a Tokyo Environmental White Paper, although the maximum concentration of photochemical oxidants recorded during daytime hours (5 a.m to 8 p.m.) in 1999 was 0.173ppm, the average concentration recorded for that years was 0.026ppm. Therefore, it seems unlikely that there would be enough concentration of photochemical oxidants to cause adverse effects on pneumatic equipment.

Oxidant concentration in Tokyo, 1999



Photochemical smog emergency alert (Tokyo)



Excerpted from the web page of
Tokyo Environmental White Paper 2000