namely, 29 centistokes, at 98.6° C. and 305 centistokes at 38° C.,—compared to the usual range of 3 to 12, and 11 to 92 centistokes, respectively.

SUMMARY

Viscosity characteristics were determined on 27 long-chain plasticizers. Most of these compounds are alkyl, aryl, or glycol esters of 9(10)- or 12-monoacetoxystearic acid. It is concluded that a low viscosity at low temperatures (below 250 centistokes at −10° C.) is an essential requirement for obtaining a low stiffness temperature in a plasticized poly(vinyl chloride-acetate) copolymer (95:5). No correlation could be found between high viscosity index or low pour point and low stiffness temperature.

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Stability of Liquid Ozone in Glass and in Contact with Various Substances

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ALTHOUGH ozone is thermodynamically unstable, pure liquid ozone can be stored for long periods of time at the temperature of liquid oxygen (−183° C.) with no apparent decomposition (*6*). Kinetic data for the decomposition of solutions of ozone in carbon tetrachloride at room temperature (*1*) may be extrapolated to lower temperatures in the range −183° to −112° C., the boiling point of liquid ozone. Such extrapolations suggest, in agreement with past observations (*6*), that the rate of decomposition of pure liquid ozone in this temperature range should be immeasurably small.

However, extrapolation of kinetic data over a range which encompasses a two- to threefold variation in temperature is undesirable. Some studies have been made of liquid ozone (2-10). As an additional observation at the Lewis Research Center on the storage stability of liquid ozone in the range between −183° C. and its boiling point, samples were held in glass vials for one to a few days and the extent of any decomposition was noted.

In addition, liquid ozone was contacted with different materials and chemical compounds, and any decomposition was noted. Although some of these results have verified previous work (*7*), the stability of ozone with a number of materials and laboratory reagents was reported for the first time.

APPARATUS AND PROCEDURE

Ozone was prepared from 99.6% pure extra-dry oxygen (Matheson Co.) in an all-glass silent discharge-type ozonizer (*5*). The oxygen was passed through copper oxide at 950° C. to remove hydrocarbons and then through Drierite, Ascarite, and a trap immersed in dry ice and acetone before it entered the ozonizer. After passing through a second dry ice–acetone trap, the ozone-oxygen mixture was condensed in a glass receiver cooled by liquid oxygen. A schematic diagram of the ozone concentration and purification apparatus is shown in Figure 1. The oxygen was pumped off through a trap filled with crystalline, metal aluminosilicates (Molecular Sieves, Type 5A, 1/16-inch pellets, Linde Air Products Co.), which destroyed any ozone vapors passing through with the oxygen. The last traces of oxygen were eliminated by vaporization and recondensation of the ozone followed by pumping until the pressure was 0.1 mm. of mercury, the vapor pressure of ozone at −183° C. (*7*). Ozone in 2- to 3-ml. quantities not needed for immediate use was stored indefinitely in a liquid nitrogen bath.

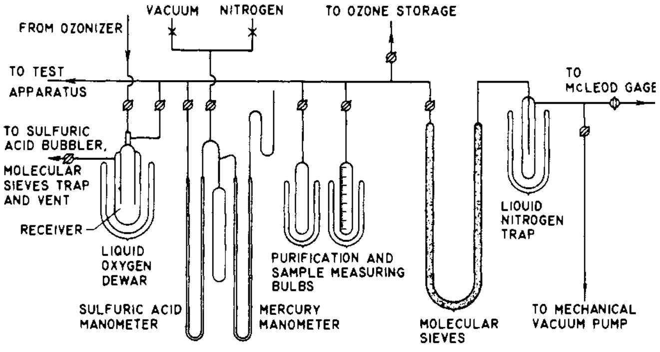

Figure 1. Ozone concentration and purification apparatus

Figure 2 shows the test apparatus and associated equipment, which was designed to operate over the temperature range of −183° to −110° C. The test bulb was immersed in a 2-liter Dewar vessel, which was cooled by a refrigerated stream of air dried by passage through an alumina column and a liquid nitrogen–cooled trap. Precooling of the airstream took place in a coil immersed in a dry ice–acetone bath, and final cooling in a U-tube immersed in liquid nitrogen in a 4-liter Dewar vessel. The temperature could be regulated by varying the airflow rate and by immersing the U-tube. A liquid nitrogen-level device to control this immersion is shown in Figure 2. A cork float opened and closed an electrical circuit, shutting off or admitting liquid nitrogen to the 4-liter Dewar vessel. The cold dry air was discharged upward in the Dewar test vessel from a perforated ring.

The temperature in the Dewar test vessel could be maintained to within 2° of the desired temperature by infrequent slight adjustments of the liquid nitrogen-level control. However, over the 15-hour periods of inattention the temperature varied as much as 10° from the set value. A temperature gradient of 10° existed between the bottom and top of the Dewar test vessel with an air flow of 15 to 20 liters per minute.

Before each run, the test bulb and any added metal were cleaned thoroughly and assembled in the Dewar test vessel. Carbon tetrachloride, dichromate-sulfuric acid cleaning solution, and distilled water were used for cleaning. Ozone was measured out in 0.5-ml. samples in the purification apparatus and transferred to the test bulb at −196° C. The bulb was evacuated to 0.1 mm. of mercury pressure and then isolated. The temperature was permitted to rise to the desired value and the cooling air flow set. Every 4 hours the temperature and pressure were read. As the pressure varied, the volume was kept constant by admission or withdrawal of mercury from the manometer.

The apparatus for observing the behavior of various chemicals with ozone is shown in Figure 3. The material to be tested was placed in the right-side bulb before the test apparatus was connected to the ozone manifold and evacuated. A 0.1-ml. sample of ozone was condensed by liquid nitrogen in the left bulb. For liquid ozone tests the ozone was transferred to the material in the right-side bulb by liquid oxygen. Contact between the ozone and test material was maintained for 1/2 hour at −183° C.; stopcocks S_1 and S_2 were opened and the resulting pressure, if any, was read on the sulfuric acid manometer in the purification apparatus (Table III, step A).

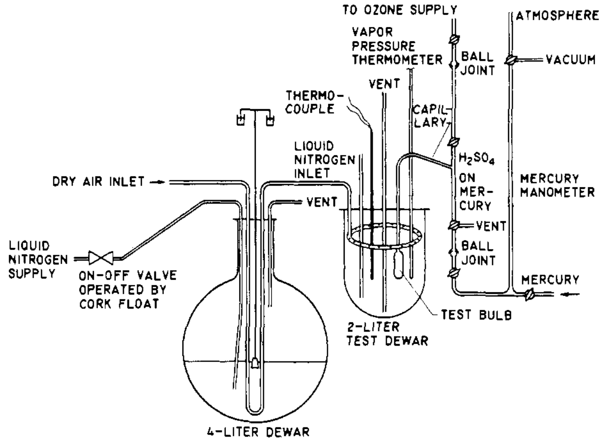

Figure 2. Decomposition testing apparatus

The test bulbs with the ozone still in the one on the right were evacuated to 0.1 mm. of mercury. Then the liquid oxygen bath was removed from the right-side bulb and the ozone was transferred back to the left bulb by cooling it with liquid nitrogen. This transfer required from 3 to 5 minutes. Stopcocks S_1 and S_2 were again opened and any oxygen pressure in the test bulbs was noted as before (Table III, step B).

Instead of being condensed on the material in the room temperature exposure tests, the 0.1-ml. of ozone was permitted to vaporize into both arms to approximately atmospheric pressure. After 15 minutes a liquid nitrogen bath was placed on the left arm and the remaining ozone condensed. The remaining oxygen pressure was read on the same manometer used in the liquid tests.

RESULTS AND DISCUSSION

The results of the decomposition tests are listed in Table I. Runs 1 to 9 were conducted in a 4-ml. glass bulb without any other material present. There was a small amount of decomposition in every run. The per cent of decomposition was calculated from the pressure due to decomposition. This pressure was obtained by subtracting the vapor pressure of ozone from the observed pressure of the test sample at the temperature of measurement. Perhaps all of the measured decomposition could be attributed to the ozone vapor in the capillary tube leading to the manometer. Decomposition of ozone in the liquid phase at temperatures below −112° C. is extremely slow or nonexistent.

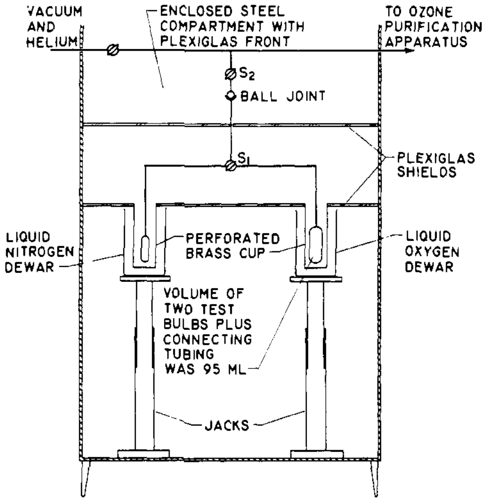

Figure 3. Apparatus for observing the behavior of chemicals with ozone

Table I. Decomposition of Ozone in Glass[a]

Run	Average Temp., ° C.	Time, Hr.	% Decompd.	% Decompn./ 24 Hr.
1	−160	20	0.01	0.01
2	−155	4	0.02	0.12
3	−152	37	0.03	0.02
4	−150	26	0.05	0.05
5	−145	65	0.03	0.01
6	−129	17	0.08	0.12
7	−120	23	0.09	0.09
8	−112	19	0.07	0.09
9	−112	43	0.35	0.20

[a] Conditioned with 30 mm. of ozone for 5 min at 25° C.

Runs 10 to 17 (Table II) were made using a 57-ml. bulb, and an added material was used in 11 to 17; three runs (11, 12, and 14) gave an amount of decomposition comparable with the runs in the 4-ml. bulb. Runs 10, 13, and 15 yielded total pressures that were less than the vapor pressures of ozone at the observed temperatures. These unrealistic results were probably caused by experimental errors in the reading of the temperatures. A reading higher than the actual value would lead to a negative decomposition pressure. Nevertheless, the conclusion is that no decomposition was caused by the added material.

Two materials caused explosions, spongy nickel (run 16) on initial exposure and a sample of aluminum (run 17) after 13 hours. The latter explosion occurred soon after a reading had been taken.

The following reagent grade materials caused no measurable decomposition of ozone during 1/2-hour storage tests at −183° C. or during subsequent separation of ozone:

Table II. Decomposition of Ozone with Added Material

Run	Compatibility Material	Av. Temp., ° C.	Time, Hr.	% Decompd.	% Decompn. per 24 Hr.
10	None	−120	60	[a]	
11	Copper	−118	87	0.46	0.13
12	Lead	−123	84	0.78	0.22
13	NaCl	−108	84	[a]	
14	Aluminum	−114	62	1.34	0.52
15	Magnesium	−114	60	[a]	
16	Nickel, spongy[b]	. . .	0 (exploded)	. . .	
17	Aluminum	−145	13 (exploded)	[a]	

[a] Pressure readings less than vapor pressure of ozone.
[b] Sample was not cleaned.

Iron, powdered
Nickel, spongy, previously exposed to O_3
Zinc, pellets
Silica gel
Polyethylene
Molecular Sieves
Bismuth, crystals
Carbon black
Calcium boride, finely crushed
Calcium hydride
Silicon carbide
Starch, potato
Potassium bromide, small crystals
Sucrose
Vanadium pentoxide, fine granular
Iodine
Hydroxylamine hydrochloride
Aluminum chloride, hydrated
Aluminum acetate
Aluminum fluoride
Naphthalene
Lithium perchlorate
Lithium hydride
Lithium borohydride
Lithium sulfate, hydrated
Lithium nitrate
Ammonium perchlorate

Materials which did cause some decomposition of ozone either during the 1/2-hour storage tests at −183° C. (step A) or during the separation of the ozone (step B) are listed in Table III. Liquid ozone was unreactive towards the paraffin hydrocarbons, ethane and propane, in a quiescent state at −183° C. but exploded when an attempt was made to separate the mixtures. With the olefins, ethylene and isobutene, ozone exploded on contact at −183° C. However naphthalene did not react. Many materials such as some hydrides, borohydrides, and starches that might be expected to react with ozone do not do so with the liquid phase.

Table III. Effect of Chemicals[a] on Ozone

	Pressure Rise, Mm. of H_2SO_4	
	Step A[b]	Step B[c]
1. Nickel, spongy (fresh)	3	6
2. Alumina, activated	0	6
3. Manganese dioxide, powdered	17	48
4. Aluminum ethoxide	91	Exploded
5. Ethylene	Exploded	
6. Propane	0	Exploded
7. Isobutene	Exploded	
8. Ethane	0	Exploded
9. Lithium peroxide	3	26
10. Charcoal, activated	Exploded	

[a] Reagent grade.
[b] Contact between 0.1 ml. of ozone and test material for 1/2 hour at −183° C.
[c] Ozone transferred from test material to bulb cooled in liquid nitrogen.

Surface conditions of the materials are important in causing ozone to decompose. Carbon black had no effect on liquid ozone, but activated charcoal caused an immediate explosion. Spongy nickel decomposed liquid ozone to a slight extent when fresh, but a sample previously exposed to ozone had no further effect.

Of the materials tested with liquid ozone, 14 were also tested with gaseous ozone for 15 minutes at room temperature (Table IV). Zinc, calcium boride, sucrose, aluminum fluoride, and lithium perchlorate did not cause the gaseous ozone to decompose much faster than in the apparatus alone. Silica gel, which is known to adsorb ozone readily, actually inhibited the decomposition to a slight extent. The other materials tested caused appreciable decomposition, and lithium borohydride initiated an explosion.

Table IV. Behavior of Gaseous Ozone with Various Substances

Material[a]	Residual Pressure[b], Mm. Hg.
1. Blank	9
2. Iron, powdered	46
3. Zinc, pellets	10
4. Silica gel	6
5. Alumina, activated	47
6. Molecular Sieves	69
7. Calcium boride, finely crushed	16
8. Sucrose	11
9. Aluminum fluoride	15
10. Lithium peroxide	70
11. Lithium perchlorate	19
12. Lithium hydride	64
13. Lithium borohydride	Exploded after 8 min.
14. Carbon black	55

[a] Reagent grade.
[b] After contact at room temperature for 15 minutes followed by condensation at −196° C.

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