INVESTIGATIONS
of
ANTI-FREEZE PREPARATIONS
(Ethylene Glycol Type)

by

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CODE

Z = Zerex.	E. I. DuPont de Nemours & Co. Wilmington, Delaware
F = Frigitone	The Firestone Tire & Rubber Co. Akron, Ohio
P = Prestone	National Carbon Co. New York, N. Y.
E.G. = Pure Ethylene glycol	Carrier Stephens Co. Lansing, Michigan

INVESTIGATION OF ANTI-FREEZE PREPARATIONS

(Ethylene Glycol Type)

Samples of commercial automobile anti-freeze preparations of the ethylene glycol type were submitted to the Research Laboratory for investigation. Three different brands were included, labeled P, F and S. In addition, some chemically pure ethylene glycol was obtained for comparison.

The following investigations were made of all four materials:

1. Freezing points at definite concentrations by volume.
2. Corrosion of metals and rubber at 50% concentration at 150°F. in 24 hours.
3. Variations in acidity.
4. Fractional distillation of the materials as received.
5. Quantities of solid residue and ash.

The materials as received exhibited the following physical properties:

Ethylene glycol: clear, water white, transparent, no suspended material. Viscosity about 2 1/2 times that of the three commercial preparations. Specific gravity was 1.0970 at 25/25.

P: dark green, contained considerable brown, waxy sediment which settled out and coated the container. Specific gravity was 1.1108 at 25/25.

F: blue, clear, transparent, no sediment or suspended material. Specific gravity was 1.1019 at 25/25.

Z: yellowish-orange, translucent, fairly clear, no perceptible sediment, very slight turbidity. Specific gravity was 1.1207 at 25/25.

Results.

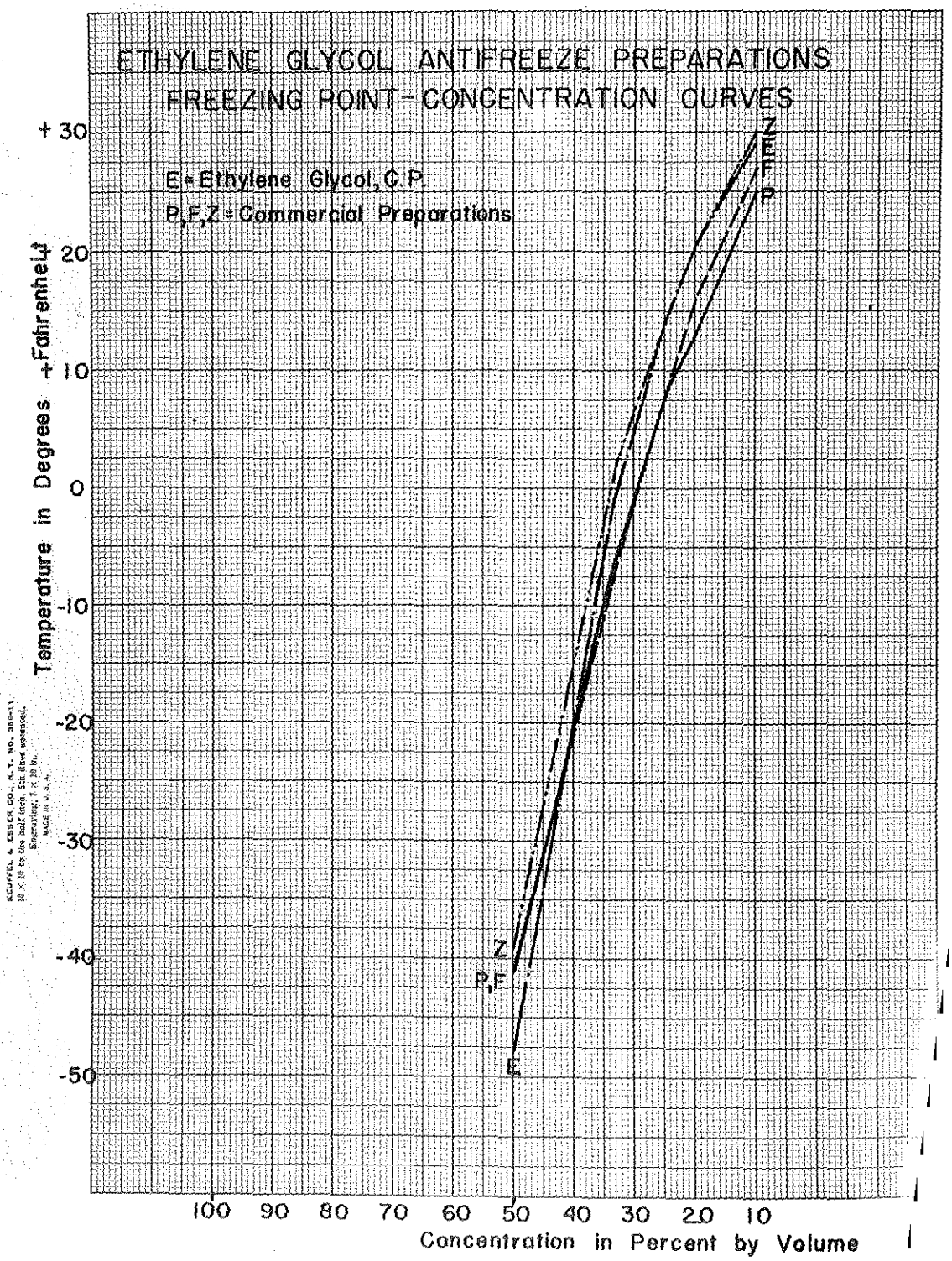
1. Freezing points. Freezing point determinations were made at the following concentrations by volume: 10%, 20%, 25%, 33 1/3% and 50%. Results are given in the following table:

TABLE I

FREEZING POINT DETERMINATIONS IN DEGREES FAHRENHEIT.

Material	Concentration by Volume, Percent.				
	50	33 1/3	25	20	10
Ethylene glycol, C. P.	-48	-1	+14	+20.5	+29
F	-41	-5	+ 9	+13	+25
F	-41	-7	+ 8	+15	+27
Z	-39	+2	+14	+20.6	+30

Data from Table I are plotted in the accompanying chart.


ETHYLENE GLYCOL ANTIFREEZE PREPARATIONS
FREEZING POINT-CONCENTRATION CURVES
E = Ethylene Glycol, C.P.
P,F,Z = Commercial Preparations
Temperature in Degrees +Fahrenheit
+30
+20
+10
0
-10
-20
-30
-40
-50
Z
P
Z
P,F
E
100 90 80 70 60 50 40 30 20 10
Concentration in Percent by Volume

2. Corrosion of Metals and Rubber. Each material was diluted to 50% by volume and placed in a large Pyrex beaker. A sample of each of the following materials was immersed completely in each solution: (a) automobile radiator rubber hose purchased in 1945 (black), (b) automobile radiator rubber hose purchased in 1941 (red), (c) steel of the type used in the manufacture of cells, and (d) pure commercial solder (no core).

All samples of metals were weighed before immersion. All samples of rubber hose were measured for wall thickness before immersion, it being accepted that swelling of rubber is nearly always an accompaniment of initial attack by solvents.

All beakers and their contents were placed in the oven at 180° F. and kept there for twenty-four hours. Loss of water due to evaporation was made up by periodic simultaneous additions of water during this period. It was observed that the solution of sample P evaporated only 50% as much as those of the other samples overnight.

After twenty-four hours the samples were removed from the oven. The inside of the beaker containing sample P was coated with a brown soot and the solution of ethylene glycol, C. P., was now quite turbid and light brown in color. No other visible changes were apparent among the four samples.

The samples of rubber and metals were removed from the beakers immediately and rinsed with distilled water. The rubber samples were placed on blotting papers and allowed to surface dry, whereupon their wall thicknesses were again measured. The metal samples were dried in the oven at 180° F., allowed to cool to room temperature and weighed. Results are shown in Tables II, III and IV.

TABLE II

ATTACK ON RUBBER HOSE

Type of Hose	Wall Thickness in Inches				
	Original	X.	Y.	Z.	W.
Black (1943)	0.175	0.190	0.190	0.189	0.189
Red (1941)	0.178	0.214	0.207	0.208	0.211

TABLE III

ATTACK ON STEEL

Material	Weight in Grams	
	Original	Final
Ethylene glycol, C.P.	4.6104	4.6037 (Black)
P	5.6940	5.6944
S	5.2980	5.2980
T	4.2786	4.2782

TABLE IV

ATTACK ON SOLDER

Material	Weight in Grams	
	Original	Final
Ethylene glycol, C. P.	4.0376	4.0373
P.	5.4664	5.4643
P.	4.8114	4.8114
P.	5.4505	5.4498

It is seen from the results indicated in Tables III and IV that the ethylene glycol dissolves steel and that solution of sample P dissolves solder. Accordingly chemical tests were undertaken to recover these materials from the respective solutions. In the case of ethylene glycol, a solution of potassium ferrocyanide was added to a portion of theethylene glycol from the beaker after the twenty-four hour corrosion test. Prussian blue was formed, indicating the presence of iron in solution. This test was negative on the material as received.

A portion of the solution of sample P in the beaker suspected of having dissolved one or both ingredients of solder (lead or tin) was treated with hydrogen sulfide gas. A precipitate was formed which was wholly soluble in hydrochloric acid. This ruled out the presence of tin in solution. Acetic acid and potassium dichromate were added to the dissolved precipitate and yellow lead chromate was formed. This proves that solution P dissolved lead from the solder but without attack on the tin.

3. Variations in Acidity. The acidity of all 50% solutions used in the corrosion investigation were taken both before and after the investigation. These are given in Table V.

TABLE V

ACIDITY AS p H OF SOLUTIONS USED IN CORROSION INVESTIGATION

Solution	Acidity as p H	
	Before Tests	After Tests
Ethylene glycol	6.58	6.38
P	8.70	7.75
F	8.65	7.80
S	8.50	7.50

4. Fractional Distillation of the Materials as Received. This investigation was conducted in the bituminous Laboratory. Results are shown in Table VI.

TABLE VI

FRACTIONAL DISTILLATIONS

Amount Distilled over in cc	Temperature in Degrees F.			
	L. C.	1	2	3
First drop	380	396	395	395
25	390	395	399	399
50	390	400	401	399
100	390	402	401	402
150	390	405	402	402
200	390	409	402	402
250	390	409	402	402
300	390	411	411	409
350	390	415	418	Split

5. Quantities of Solid Residue and Ash. This investigation was also conducted in the bituminous laboratory. Results are shown in Tables VII and VIII.

TABLE VII

QUANTITIES OF ASH IN SAMPLES AS RECEIVED

Material	Ash in Percent	
Ethylene glycol	0.00	
P	0.02	(Fe_2O_3)
F	0.03	(Zn_2O)
Z	0.49	(Na_2O)

TABLE VIII

QUANTITIES OF VOLATILE MATTER DRIVEN OFF AT 750°C IN SAMPLES AS RECEIVED

Material	Moisture in Percent	
Ethylene glycol	0.00	
P	0.00	
F	1.7	(Zn,P)
Z	2.1	(Zn,P)

During investigations (4) and (5) it was noted that the wax-like material contained in sample P was volatile and distilled over into the distillate breaking colorless during the transition. Its original color is thought possibly due to the iron which was recovered in the ash. The distillate was turbid.

Upon redistilling the distillates of samples P, F and Y these liquids were found to distil within 2 degrees F. from start to finish, namely from 404° to 406° F.

It was also found that all three commercial brands evaporate at the rate of 5 grams per square inch (of surface area) in 24 hours at 100° C.

Conclusions.

All things considered, material F would seem to be the best product. Material P offers only slightly greater protection against freezing than does material F, but P dissolves the lead in solder and has a greater attack on one type of rubber hose used in the investigation. Whether these attacks are sufficiently serious to warrant not using the product on their account is, of course, a matter of opinion.

Both P and F offer greater protection against freezing at temperatures above -22° F than does pure ethylene glycol. Material Y offers the least protection at all temperatures, and its effect on one type of rubber was nearly as great as that of ethylene glycol.

TABLE IX

SUMMARY OF SIGNIFICANT DATA

Material	Specific Gravity	Freezing Point in Deg. F., 1/3 con.	Corrosion of Metals Loss in Grams		Swelling of Rubber Increase in Wall Thickness in Inches		Rate of Evaporation Loss in Grams per Square Inch in 24 Hours at 100° C.
			Steel	Lead	Sample 1941	Sample 1945	
E. G.	1.0870	-1	-.0065	.0000	.044	.015	5.0
P	1.1108	-8	.0000	-.0021	.057	.015	5.0
F	1.1019	-7	.0000	.0000	.052	.014	5.0
Z	1.1207	+2	.00000	.0000	.041	.014	5.0