CCL REPORT NO. 300

FINAL REPORT

STORAGE STABILITY OF BRAKE FLUIDS IN TIN, STEEL AND GLASS CONTAINERS

BY

CHARLES B. JORDAN

JANUARY 1972

U. S. ARMY
ABERDEEN RESEARCH & DEVELOPMENT CENTER
COATING & CHEMICAL LABORATORY
Aberdeen Proving Ground
Maryland

17

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U.S. Army Aberdeen Research & Development Center Coating & Chemical Laboratory Aberdeen Proving Ground, Maryland 21005	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

STORAGE STABILITY OF BRAKE FLUIDS IN TIN, STEEL AND GLASS CONTAINERS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Report

5. AUTHOR(S) (Last name, first name, initial)

Jordan, Charles B.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
January 1972	17	6

8a. CONTRACT OR GRANT NO. AMCMS Code No. 502E.11.80200 b. PROJECT NO. 1T062105A108 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) CCL #300 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. AVAILABILITY/LIMITATION NOTICES

This document has been approved for public release and sale; its distribution is unlimited. Qualified requesters may obtain copies of this report from Defense Documentation Center.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	U.S. Army Materiel Command Washington, D. C. 20315

13. ABSTRACT

The object of this study was to compare the storage stability of hydraulic brake fluids in tin, steel and glass containers.

Thirty brake fluids approved under Federal Specification VV-B-680 were stored in 5 gallon steel drums, 1 gallon tin cans, and 1/2 gallon glass jugs for a period of 5 years. Periodically, corrosion and oxidation stability tests were conducted on the fluids. Sediment formation was observed.

After storage for one year, an average of three fluids failed the corrosion test and six failed to meet the oxidation stability requirement. After five years the average number of failures increased to fifteen for the corrosion test and twenty for the oxidation stability test. Only four samples showed more than 0.05% sediment by weight, none of the samples showed more than 0.10%. There was no discernible pattern regarding commonality of failure under these test conditions.

The oxidation stability and corrosiveness results indicate that a storage stability requirement, which would screen out those fluids whose antioxidant and corrosion inhibitor combinations are not stable over specified storage periods, should be added to all brake fluid specifications.

DD FORM 1 JAN 64 1473

UNCLASSIFIED

Security Classification

DDC AVAILABILITY NOTICE

Qualified requesters may obtain copies of this report from Defense Documentation Center, Cameron Station, Alexandria, Virginia 22314

THE FINDINGS IN THIS REPORT ARE NOT TO BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, UNLESS SO DESIGNATED BY OTHER AUTHORIZED DOCUMENTS.

DESTROY THIS REPORT WHEN IT IS NO LONGER NEEDED. DO NOT RETURN IT TO THE ORIGINATOR.

UNCLASSIFIED

CCL REPORT NO. 300

FINAL REPORT

STORAGE STABILITY OF BRAKE FLUIDS IN TIN, STEEL AND GLASS CONTAINERS

BY

CHARLES B. JORDAN

JANUARY 1972

AMCMS CODE NO. 502E.11.80200

DEPARTMENT OF THE ARMY PROJECT NO.
1T062105A108

U.S. ARMY ABERDEEN RESEARCH AND DEVELOPMENT CENTER
COATING AND CHEMICAL LABORATORY
ABERDEEN PROVING GROUND
MARYLAND 21005

UNCLASSIFIED

ABSTRACT

The object of this study was to compare the storage stability of hydraulic brake fluids in tin, steel and glass containers.

Thirty brake fluids approved under Federal Specification VV-B-680 were stored in 5 gallon steel drums, 1 gallon tin cans, and 1/2 gallon glass jugs for a period of 5 years. Periodically, corrosion and oxidation stability tests were conducted on the fluids. Sediment formation was observed.

After storage for one year, an average of three fluids failed the corrosion test and six failed to meet the oxidation stability requirement. After five years the average number of failures increased to fifteen for the corrosion test and twenty for the oxidation stability test. Only four samples showed more than 0.05% sediment by weight, none of the samples showed more than 0.10%. There was no discernible pattern regarding commonality of failure under these test conditions.

The oxidation stability and corrosiveness results indicate that a storage stability requirement, which would screen out those fluids whose antioxidant and corrosion inhibitor combinations are not stable over specified storage periods, should be added to all brake fluid specifications.

TABLE OF CONTENTS

I. INTRODUCTION

Two of the more important requirements for hydraulic brake fluids supplied to the Government under Federal Specification VV-B-680 are that they must be non-corrosive in brake systems and exhibit oxidation stability on extended use or storage. Tests for measuirng these criteria are included in the specification and conducted at the time of qualification.

Brake fluids are composed of many combinations of base lubricants, solvents and inhibitors. In current fluids base lubricants are generally polyglycols or castor oil derivatives; solvents are glycols, glycol-ethers, or alcohols; inhibitor combinations include alkaline materials and antioxidants. Upon storage, the corrosion inhibitors may interact, deteriorate, or become depleted by contact with metals in the containers, by presence of water and oxidation products in the fluid, or by fluctuating temperatures. If the inhibitors are consumed, corrosion may then take place.

Studies over the past two decades have shown a marked improvement in storage stability of brake fluids (LSD Report Nos. 145, 187 and CCL Report No. 176).

This report contains the results of a continuing program of monitoring the storage stability of fluids approved for use in Government vehicles.

II. DETAILS OF TEST

A. Brake Fluids Tested. All brake fluids appearing on the Qualified Products List for Federal Specification VV-B-680 at the beginning of the test were used in the program. There were 30 fluids from 9 different manufacturers. All fluids met specification requirements at the time of qualification.

B. Type of containers. Three types of containers were used as follows:

1. One-half gallon amber glass jugs with handles, closed by a plastic lid with an organic coated cardboard inner seal.

2. One gallon tin cans made of 0.5 electrolytic tin plate, fabricated with 60 lead/40 tin solder. These cans are "dry-doped" and of the type used in packaging brake fluids. The cans were closed by tin inner seals (until the time of the first inspection) and a screw-cap tin lid containing an organic coated cardboard inner liner.

3. Five gallon unlined steel pails used by the brake fluid manufacturers for packaging and shipping brake fluid. The pails met Federal Specification PPP-P-704, Type I. They were generally equipped with metal or polyethylene pouring spouts and closed by screw cap tin lids containing metal or organic lined cardboard inner seals.

C. Storage Data. The glass, tin, and steel containers were stored in an unheated warehouse for the entire 5 year storage period (average ambient temperatures at APG are included in Table IV). Samples were removed for test after 1 year, 2-1/2 years and 5 years. Unless otherwise stated containers were immediately resealed.

D. Tests Conducted.

1. Corrosion Test. All fluids were subjected to the corrosiveness test outlined in paragraph 4.6.11 of Federal Specification VV-B-680 after completion of the designated storage periods. This test consists of the immersion of a set of six different metal strips in electrolytic contact in the fluid being tested, and heating at 100°C. (212°F.) for 120 hours. On completion of the test weight loss of the metal specimens is measured and visual evidence of corrosion is noted.

2. Oxidation Stability Test. All fluids were subjected to the oxidation stability test specified in paragraph 4.6.14 of Federal Specification VV-B-680, at the end of the specified storage periods. This test consists of the partial immersion of a set of aluminum and cast iron test specimens electrolytically coupled in a sample of the fluid. 0.2% benzolperoxide and 5.0% water is dissolved in the fluid. The test specimens are immersed for 3 days at room temperature and then held for 7 days at 70°C. (158°F.), after which weight loss is measured and visual evidence of corrosion noted.

3. Water Tolerance Test. All fluids were subjected to the water tolerance test specified in paragraph 4.6.9 of Federal Specification VV-B-680. This test was conducted after 5 years storage only. It consists of exposing a sample of the fluid containing 3-1/2% water to a temperature of -40°C. (-40°F.) for 24 hours followed by exposure of the sample to a temperature of 60°C. (140°F.) for 24 hours. Evidence of separation or stratification is noted and the amount of sediment is determined in accordance with ASTM Method D-91.

4. Sediment Determination. The volume of sediment in the packaged fluids was determined after 5 years storage. The containers were well-shaken and samples were tested in accordance with ASTM Method D-91.

III. RESULTS OF TESTS

A. Corrosion Tests - (Table I).

1. Tin Containers. After one year 2 fluids failed; after 2-1/2 years 4 fluids failed; and after 5 years 13 fluids failed. Most failures occurred on brass and aluminum test specimens.

2. Glass Containers. After one year 4 fluids failed, after 2-1/2 years 5 fluids failed; and after 5 years 13 fluids failed. In the glass containers, brass and copper test specimens accounted for most of the failures.

3. Steel Containers. After one year 4 fluids failed; after 2-1/2 years 6 fluids failed; and after 5 years eight fluids failed. These values represent the least failures in corrosion tests found in any of the containers. Tin, brass and copper test specimens were the most prevalent failing metals in steel containers.

Fluids from each brake fluid manufacturer were included among the failing fluids in each of the three containers.

B. Oxidation Stability Tests (Table II).

1. Tin Containers. After 1 year, 7 fluids failed the oxidation stability test in tin containers. After 2-1/2 years only 3 fluids were found to fail, but after 5 years 14 fluids failed. The cast iron test specimens failed more often than the aluminum.

2. Glass Containers. After 1 year and 2-1/2 years there were 5 failing fluids. All of these failures were on the aluminum specimen. After 5 years, 17 fluids failed of which 5 failed aluminum, 7 failed cast iron, and 5 failed both metals.

3. Steel Containers. After 1 year 7 fluids failed; after 2-1/2 years 16 fluids failed, and after 5 years, 25 fluids failed in the steel containers. Failures on the aluminum test specimens occurred in the first 2-1/2 years while the majority of the cast iron failures occurred after 5 years.

As was found in the corrosion tests, fluids from each manufacturer were included among the failing fluids in each of the three containers in the oxidation stability tests.

C. Sediment in the Fluids and Sediment after the Water Tolerance Tests (Table III).

1. Tin Containers. In the tin containers only one fluid showed greater than 0.05% sediment (#24 showed 0.07%). Also only one fluid showed greater than 0.05% sediment after the water tolerance test (#20 showed 0.08%).

2. Glass Containers. In the glass containers no fluid showed a measurable amount of sediment. After the water tolerance one fluid (#21) showed 0.10% sediment. No other fluid showed more than a trace.

3. Steel Containers. More sediment was found in the fluids stored in steel containers than was found in the fluids stored in tin and glass. Three fluids showed greater than 0.05% sediment (#22, #24, and #28 showed 0.10% sediment). After the water tolerance test #21 and #22 showed 0.10% sediment. All others showed less than 0.05% sediment.

IV. DISCUSSION

A comparison of test results with the results received at the time the fluids were originally qualified showed that in most fluids there was evidence of progressive inhibitor depletion upon storage, even though several of the fluids still met the minimum requirements of the specification. Recent brake fluid rulings issued by the National Highway Safety Bureau, Dept. of Transportation, state that brake fluid offered for sale to the public must meet certain minimum physical and chemical requirements as set forth in the D.O.T. Specification regardless of the date of manufacture of the fluid. In addition it would be undesirable from the military point of view to have a brake fluid in a vehicle which would not give satisfactory performance after limited standby storage. Results included in this report indicate that there is still a storage problem, and a comprehensive effort should be made by industry and the Government to overcome instability of brake fluid upon aging.

Federal brake fluid specifications are "performance" specifications and brake fluids meeting these specifications, as stated in the introduction, are composed of many combinations of base lubricants, solvents, and inhibitors. The inhibitors, usually reactive antioxidants and alkaline materials, interreact, deteriorate or become depleted. Subsequently, the solvents and base lubricants are free to oxidize to terminal organic acid molecules which attack and corrode the metal components of the brake system. Metal soaps are formed which account for gum buildup in the system, and malfunction of the brake system frequently occurs.

It is possible to prepare brake fluids which are satisfactory after 5 years' storage, as indicated by the test results in the tables. Also, the overall stability of brake fluids in storage and in use has markedly increased in recent years due to the presence of oxidation stability requirements in the specifications of both Government and Industry.

The results of this study will be brought to the attention of brake fluid suppliers and the automotive industry so that further investigation in the area of brake fluid stability can be made.

V. RECOMMENDATIONS

It is recommended that investigation continue on factors causing brake fluid instability and that an attempt be made to correlate brake fluid composition with fluid stability.

Based on the present study it is recommended that brake fluid be packaged in tin containers, preferably of small volume. This will decrease chance of contamination and moisture pickup, and increase "turn-over" of stored fluid.

It is recommended that a long term stability requirement be added to brake fluid specifications. It is further recommended that periodic inspection of stored fluids be accomplished and only those fluids found to be stable at the time of inspection be retained for use in military vehicles.

IV. ACKNOWLEDGEMENT

The assistance of Mr. H. R. Sheets in accumulating the test data included in this report is gratefully acknowledged.

V. REFERENCES

1. Federal Specification VV-B-680a, Brake Fluid Automotive, dated 18 18 October 1967.

2. Federal Specification PPP-P-704, Pails, Metal: (Shipping, Steel, 1 through 12 Gallons) dated 16 August 1960.

3. ASTM Method D-91, Precipitation Number of Lubricating Oils.

4. LSD Report No. 145, Evaluation of Hydraulic Brake Preservative Compounds after 5 Years Storage, dated 24 January 1952.

5. LSD Report No. 187, Development of a Stability Test for Hydraulic Brake Fluids, dated 23 March 1953.

6. CCL Report No. 176, Preliminary Studies on the Storage Stability of Brake Fluids, dated 23 February 1965.

APPENDIX A

Preceding page blank

TABLE I

Results of Corrosion Tests on Brake Fluids After Storage in Various Containers

Sample No.	Tin 1 Yr.	Tin 2-1/2 Yrs.	Tin 5 Yrs.	Glass 1 Yr.	Glass 2-1/2 Yrs.	Glass 5 Yrs.	Steel 1 Yr.	Steel 2-1/2 Yrs.	Steel 5 Yrs.
1	B	OK	OK	OK	OK	OK	OK	OK	OK
2	OK	OK	OK	OK	OK	OK	OK	OK	OK
3	OK	OK	F	OK	OK	OK	OK	OK	OK
4	OK	OK	OK	OK	OK	F	OK	OK	OK
5	OK	OK	OK	OK	OK	OK	OK	OK	OK
6	B	OK	OK	OK	OK	OK	OK	OK	OK
7	OK	OK	OK	OK	OK	OK	OK	OK	OK
8	OK	OK	OK	OK	OK	OK	OK	OK	OK
9	OK	OK	B	OK	OK	B	--	--	--
10	OK	B	OK	B	OK	B	B	OK	F
11	OK	F	F	F	F	F	OK	OK	F
12	OK	OK	F	OK	OK	F	OK	OK	OK
13	F	F	F	B	OK	F	OK	OK	OK
14	OK	OK	F	OK	OK	F	B	B	OK
15	OK	F	F	OK	F	F	F	F	F
16	OK	OK	OK	OK	OK	F	OK	OK	OK
17	OK	OK	OK	OK	OK	OK	--	--	--
18	B	OK	F	F	F	F	F	F	F
19	OK	OK	F	OK	OK	F	OK	OK	OK
20	OK	OK	OK	B	B	OK	OK	OK	OK
21	OK	OK	F	OK	OK	OK	OK	OK	OK
22	OK	OK	OK	OK	OK	OK	B	F	F
23	OK	OK	B	F	F	F	OK	B	OK
24	OK	OK	OK	OK	OK	OK	OK	B	OK
25	OK	OK	F	OK	OK	F	F	F	F
26	B	OK	F	OK	OK	F	OK	F	OK
27	OK	OK	F	F	OK	B	OK	OK	F
28	OK	B	OK	OK	OK	OK	OK	OK	OK
29	OK	OK	OK	--	--	--	OK	OK	OK
30	F	F	F	OK	F	F	F	F	F

Legends: B = Borderline; F = Fail.

TABLE II

Results of Oxidation-Stability Tests on Brake Fluids After Storage in Various Containers

Sample No.	Tin 1 Yr.	Tin 2-1/2 Yrs.	Tin 5 Yrs.	Glass 1 Yr.	Glass 2-1/2 Yrs.	Glass 5 Yrs.	Steel 1 Yr.	Steel 2-1/2 Yrs.	Steel 5 Yrs.
1	OK	F	F	OK	OK	F	OK	F	F
2	OK	OK	F	OK	OK	F	OK	F	F
3	OK	OK	F	OK	OK	OK	OK	F	F
4	OK	OK	OK	OK	OK	F	OK	F	F
5	OK	OK	OK	OK	OK	OK	OK	OK	F
6	OK	OK	F	OK	OK	F	OK	OK	F
7	OK	OK	OK	F	F	OK	OK	F	F
8	OK	OK	F	OK	OK	OK	OK	OK	F
9	OK	OK	F	OK	OK	OK	--	--	--
10	OK	OK	F	OK	OK	F	OK	OK	F
11	OK	OK	OK	F	F	F	F	F	F
12	F	F	F	F	F	F	F	F	F
13	OK	OK	OK	OK	OK	OK	OK	F	F
14	F	OK	OK	F	F	F	F	F	F
15	OK	OK	OK	OK	OK	F	OK	F	F
16	F	OK	F	OK	OK	F	F	F	F
17	OK	F	F	OK	OK	OK	--	--	--
18	F	OK	F	F	F	F	F	F	F
19	F	OK	F	OK	OK	F	F	F	F
20	OK	OK	F	OK	OK	OK	OK	OK	F
21	F	OK	OK	OK	OK	F	OK	OK	F
22	F	OK	F	OK	OK	F	F	F	F
23	OK	OK	F	OK	OK	F	OK	F	F
24	OK	OK	F	OK	OK	OK	OK	OK	F
25	OK	OK	F	OK	OK	F	OK	OK	F
26	OK	OK	F	OK	OK	F	OK	F	F
27	OK	OK	F	OK	OK	OK	OK	OK	F
28	OK	OK	OK	OK	OK	OK	OK	OK	OK
29	OK	OK	OK	OK	OK	OK	OK	OK	OK
30	OK	OK	OK	OK	OK	OK	OK	OK	OK

Legend: F - Fail.

TABLE III

Sediment and Sediment After Water Tolerance Test on Brake Fluids After 5 Years Storage in Various Containers

Sample No.	Tin: Percent Sediment	Tin: Sediment After Water Tolerance	Glass: Percent Sediment	Glass: Sediment After Water Tolerance	Steel: Percent Sediment	Steel: Sediment After Water Tolerance
1	Trace	0.02	Trace	Trace	0.02	Trace
2	Nil	0.02	Nil	Trace	Nil	0.04
3	0.02	Trace	Nil	Trace	0.02	Trace
4	0.05	Nil	Nil	Nil	0.025	0.02
5	0.025	Nil	Nil	Nil	0.025	0.04
6	Nil	Trace	Nil	Nil	Trace	Trace
7	Nil	Nil	Nil	Nil	Nil	Trace
8	Nil	Nil	Nil	Trace	Nil	Trace
9	Trace	Nil	Nil	0.02	--	--
10	0.02	Nil	Nil	Trace	0.02	0.04
11	Nil	Nil	Nil	Nil	Trace	Trace
12	0.02	0.025	Nil	Trace	0.02	Trace
13	Nil	Nil	Nil	Nil	Trace	Nil
14	Nil	Nil	Nil	Nil	Trace	Nil
15	0.01	0.05	Nil	Trace	0.01	0.02
16	Trace	Trace	Nil	Trace	0.02	Trace
17	Trace	Trace	Nil	Trace	--	--
18	Trace	Nil	Nil	Nil	Trace	Trace
19	Trace	Nil	Nil	Trace	0.05	Nil
20	0.05	0.08	Nil	Nil	0.05	Trace
21	0.02	Nil	Nil	0.10	0.05	0.10
22	0.025	0.05	Nil	Nil	0.10	0.10
23	Trace	Nil	Nil	Nil	Trace	Trace
24	0.07	Trace	Nil	Nil	0.10	Trace
25	Trace	Nil	Nil	Nil	Nil	Nil
26	Nil	Nil	Nil	Nil	Nil	Nil
27	0.05	0.02	Nil	Nil	Trace	Nil
28	0.025	Trace	Nil	Nil	0.10	Trace
29	Nil	0.02	Nil	Nil	Trace	0.02
30	Nil	Trace	Nil	Nil	Nil	Trace

TABLE IV

Average Ambient Temperatures at
Aberdeen Proving Ground, Maryland (15 Year period)

Month	Highest Temperature, °F.	Lowest Temperature, °F.	Mean Temperature, °F.
January	72	3	32.9
February	81	3	34.7
March	86	10	42.7
April	90	13	50.5
May	97	34	61.4
June	100	40	70.6
July	103	50	75.2
August	97	49	73.1
September	96	38	68.4
October	92	25	56.1
November	79	8	44.9
December	68	5	35.5