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WATERTOWN ARSENAL LABORATORY

MEMORANDUM REPORT

NO. WAL 396/10

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EXAMINATION AND TESTS OF HYDRAULIC BRAKE FLUIDS AND DEFECTIVE BRAKE MECHANISMS

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Watertown Arsenal Laboratory
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20 August 1947

EXAMINATION AND TESTS OF HYDRAULIC BRAKE FLUIDS AND DEFECTIVE BRAKE MECHANISMS

OBJECT

The object of this report is to review the examination and tests made on two hydraulic brake fluids and six defective wheel brake mechanisms submitted by Aberdeen Proving Ground at the request of ORDTB-Fuels and Lubricants, with special consideration to the possibility of galvanic corrosion as a cause of failure of brake mechanisms.

SUMMARY

Two brake fluids and six defective wheel brake mechanisms were received and examined. One brake fluid was submitted as considered to be stable and the tests conducted indicate that in using this fluid galvanic corrosion would be negligible. The second brake fluid was submitted as considered to be unstable and the tests conducted indicate that galvanic corrosion can be present when this fluid is in use. Other tests performed indicate greater resistance to break down and less tendency toward corrosion in the case of the stable fluid.

The six brake mechanisms received were in poor condition, though all were considered operable. Corrosion covered by a thin deposit of gummy or varnish like break down product of brake fluid was present in the operating end of all cylinders. This gumming and corrosion is considered to be the result of leakage or wiping through of brake fluid, the evaporation of volatile solvents at the temperature of operation and the combined action of atmospheric moisture and dust on unsealed ends of brake cylinders.

It is recommended that some consideration be given to the use of a non-gumming inhibited mineral oil as a brake fluid and that better mechanical protection against moisture and dust be given to operating ends of wheel brake cylinders.

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INTRODUCTION

A letter (file O.O. 412.2/2180 ORDTB-Fuels & Lubricants) dated 5 February 1947 described difficulty experienced in hydraulic brake systems due to a deposit of oxidized brake fluid at the end of wheel and master cylinders exposed to the atmosphere. This deposit causes the pistons to freeze in the cylinders and occurs in brake systems of stored vehicles and in packaged assemblies coated with hydraulic brake fluid. Brown print drawings were enclosed showing the major components of a hydraulic brake system. Drawing of Part No. 924641, showing the assembly of the wheel brake cylinder, was marked with red to indicate the location of trouble. This letter requested that this Arsenal "review this problem and submit an opinion in respect to the possibility of galvanic activity at these points from the combination of materials present" and advised that representative samples of defective brake assemblies and samples of stable and unstable hydraulic brake fluids would be forwarded by Aberdeen Proving Ground. This letter also recommended that a representative of this Laboratory travel to Aberdeen Proving Ground in the event that further information or data were necessary and to review the problem with personnel at the Automotive Chemical Laboratory.

Materials were shipped by Aberdeen Proving Ground under cover letter APG 450/48, ORDBG-DPC, and six wheel cylinders secured by Aberdeen Proving Ground from trucks in "standby" storage at Letterkenny Ordnance Depot, Chambersburg, Pa. were received. Two samples of hydraulic brake fluid were included in this shipment. Preliminary examination of these materials showed the advisability of a visit to Aberdeen Proving Ground Automotive Chemical Laboratory by a representative of this Laboratory and travel was arranged to permit a conference with a representative of ORDTB-Fuels & Lubricants and the Automotive Chemical Laboratory staff at Aberdeen Proving Ground on 7 April 1947. A sample cylinder at the Automotive Chemical Laboratory exhibited large quantities of gummy material but no corrosion in the cylinder or pistons which were completely frozen in place. The personnel of the Automotive Chemical Laboratory expressed the opinion that the hydraulic brake fluids in use were the principal cause of troubles being experienced and it was agreed that examination and tests would be performed on the samples of brake fluids submitted to Watertown Arsenal while experiments were being carried on at the Automotive Chemical Laboratory to find substitute fluids which would not produce a gummy or varnish like deposit when in use.

The Brake fluids were completely used in the tests described below under "Test Procedure" and no analysis of the fluids were made. The description given in the cover letter from Aberdeen Proving Ground is as follows:- "Fluid marked Wagner 21-11 meets U.S.A. Specification 2-111b and is considered to be relatively stable. The base is reported to be of the reacted castor oil type. Fluid marked Puritan ES-377b meets specification ES-377b and is unstable. The base is reported to be of the castor oil type".

The brake cylinders were received in poor condition due to exposure to rain or snow during travel. The wheel cylinders were all made of cast iron. Five of them had aluminum pistons. The sixth had tin plated cast iron pistons. All the pistons could be moved in the cylinders by hand without difficulty.

TEST PROCEDURE, RESULTS, DATA AND DISCUSSION

Brake cylinder assemblies were examined visually and all cast iron cylinders had extensive areas of corrosion at the ends where the pistons operate. Rubbing areas of the pistons were relatively free of corrosion. One aluminum piston exhibited corrosion in the form of a ring of pitted areas near the end in contact with the rubber packing. The tin plated cast iron pistons were corroded but not to the same extent shown by cylinders. The end surface of all pistons in contact with the rubber packing was lightly etched. Some rubber packings showed evidence of leakage of fluid and were lightly glazed by evaporation of solvents from the brake fluid. Representative brake cylinders were split longitudinally, by sawing, to expose the interior and to permit photography after the removal of small deposits of gummy or varnish like material found covering the corroded areas. This gum or varnish like material was removed by washing with pyridine, the solvent evaporated and the residue was subjected to a qualitative chemical analysis by means of the spectrograph. The deposit removed from the cylinder shown in Figure 1 (WTN 720-775) contained the metals iron, silicon, aluminum, copper, cadmium, magnesium and a trace of zinc. The deposit removed from the aluminum pistons in this assembly contained the metals iron, silicon, copper, cadmium, magnesium and tin with traces of aluminum and zinc. The deposit removed from the cylinder shown in Figure 2 (WTN 720-776) contained the metals iron, silicon, aluminum, copper, magnesium, tin with trace of zinc. The deposit removed from the tin plated cast iron pistons of this assembly contained the metals iron, silicon, aluminum, copper, magnesium, traces of cadmium and zinc with a larger quantity of tin. These photographs show the typical corrosion found in all the cylinders submitted and the presence of the metals listed indicates a general corrosion of the entire brake fluid carrying system, though some traces may have been introduced from outside sources while in unprotected use in service. This corrosion is probably at least partially due to galvanic action between the several metals present in the brake system, particularly when the system is exposed to the action of moisture, as it is in the operating ends of brake cylinders. The gumming deposit is considered to be the result of leakage or wiping through of fluid by the pistons, the evaporation of the solvent portion of the fluid at the temperatures of operation, which are above the boiling points of the solvents indicated by the inclosure in the basic letter, and the action of oxygen and moisture of the atmosphere. While this combination of conditions exist in the system it is expected that this is a natural result and it is recommended that some mechanical means be taken to protect the operating ends of brake cylinders from moisture and dust.

The brake fluids submitted were subjected to tests which might indicate the breakdown of materials into fluids of corrosive nature or tendencies and included measurement of galvanic currents produced by the brake fluids both before and after breakdown tests, when possible.

Corrosion and oxidation stability were determined by the method described in Specification AXS-808 for special recoil oil, modified by the use of strips of cast iron and aluminum alloy in place of steel and copper required by the specification and the use of fifty

(50) milliliters of fluid instead of the one hundred (100) required. In this test the two metals in contact with each other are immersed in the fluid in a tube fitted with a reflux condenser. The test tube, containing the metals and the fluid, is placed in a thermostatically controlled bath maintained at 212°F. and a glass tube with inside diameter of 1 to 2 mm. is introduced through the condenser in such a manner that it extends well to the bottom of the test tube. Dry oxygen is introduced through this tube and flows at a rate of 3 plus or minus 0.2 liters per hour. The metal strips are weighed for gain or loss at the end of specified periods of time and examination of the solution is made, particularly for acid break down products represented by the neutralization number which is expressed as milligrams of potassium hydroxide required to neutralize the acid present in 1 gram of fluid. Table I lists the neutralization numbers determined through this test and while both fluids develop acidity it is significant that the Puritan ES-377b develops approximately double the acid produced in Wagner 21 - 11. Table II lists the change in weight of the metal test pieces exposed during this test with results expressed as loss or gain in milligrams per square inch. The stable fluid (Wagner 21 - 11) shows little or no change in the metal after the first twenty-four hours while the unstable fluid (Puritan ES-377b) continues to corrode the aluminum test piece, accelerating the action with increasing acid content. It should also be noted that the aluminum test piece in Puritan ES-377b fluid was non-uniformly attacked with some attack above the liquid line, probably due to bubbling or spray action of the fluid on the test piece. The gain in weight of the cast iron test pieces represents oxidation products adhering to the test pieces and is of such a small magnitude as to be considered insignificant. The stable fluid exhibited little visual change during this test. The unstable fluid became much darker in color and developed a gelatinous precipitate (due to reaction between the fluid and the dissolved aluminum). It was considered impractical to conduct galvanic tests, comparing these two solutions, on account of this precipitate and obvious decomposition of fluid.

The brake fluids were also subjected to oxidation tests in the Norma-Hoffman bomb in the manner recommended by the Annular Bearing Engineers Committee of the National Lubricating Grease Institute in Technical Bulletin No. 4, Nov. 1944 and Technical Bulletin No. 6, Jan. 1946. While this apparatus and test was primarily designed to test the storage life of greases, it was applied to these fluids in order that galvanic measurements could be made on the fluids after the test had been applied and in this way furnish some indication of corrosiveness after service conditions under pressure. The test places the fluid in a glass container inside a tight metal bomb filled with oxygen at 110 pounds per square inch gauge pressure and maintained at a temperature of 210°F. for periods up to 500 hours. The decrease of oxygen pressure with time is noted and plotted on a special graph and indicates comparative break down time of test samples. These tests were run in duplicate bombs: one pair with no metal present; one pair with a strip of aluminum alloy in each dish; one pair with a strip of cast iron in each dish; and one pair with strips of both metals in each dish. These metal test strips were approximately one half the size of those used in the corrosion and oxidation stability test. Neutralization numbers were determined on the fluid in each dish after the completion of the test and the change in weight of the metal test pieces was determined. The neutralization numbers of fluids from the Norma-Hoffman test are shown in Table III and the change in weight of metal test pieces during this test are shown in Table IV. The results of loss or gain in weight are recorded in milligrams per square inch.

No conclusions can be drawn from the results of this test as the correlation of this test with materials other than lubricating greases depends on an accumulation of data from laboratory and service tests not present in this case. It is interesting to note that

(1) under pressure and in the absence of catalyst, the stable fluid, Wagner 21-11 develops a much higher acidity than the unstable fluid, Puritan ES-377b.

(2) the developed acidity of the stable fluid drops down almost to the level of the unstable fluid when both metal catalysts are present.

(3) no significant difference is noted in the unstable fluid when metal catalysts are present.

(4) that even in the presence of lower acid values, the loss in weight of aluminum strips and the gain in weight of cast iron strips used as catalyzers are greater per unit area in the case of the unstable fluid indicating a greater tendency toward corrosion.

Graphs presented as Figure 3 and Figure 4 show the pressure drop curves of these two series of tests. A general inference may be drawn that the combination of aluminum and cast iron as present in brake cylinder mechanisms does not make the fluid less resistant to oxidation, does not stabilize the fluids with respect to resistance to oxidation.

Tendency toward galvanic corrosion was determined on both fluids in the original condition and after the oxidation test in the Norma-Hoffman bomb. This was determined by setting up a cell of fluid in which strips of cast iron and aluminum alloy were immersed and which was allowed to discharge continually through a small resistance. By measuring the potential drop across the resistance the current could be determined without interrupting or changing it. Cells with one ohm and one hundred ohm resistances were used on the original fluids. Resistances of approximately one ohm were used on fluids after the Norma-Hoffman bomb tests. The galvanic current is recorded in microamperes per square inch of metal. The data of these tests are presented in Table V for the original fluids and Table VI for the fluids after oxidation in the Norma-Hoffman Bomb tests.

In considering the data from the galvanic cells, the way the current is maintained or falls off is significant. By this criterion, the unstable fluid, Puritan ES-377b is not as desireable as the stable fluid. There is, as yet, no basis for setting a maximum limit over which the galvanic current may be called too high. Work done with aqueous solutions shows that more than five microamperes per square inch is associated with significant corrosion. This figure might be used as a rough guide for this type of solution until further experimental work yields a better value. The values determined for the stable fluid are generally under this figure while those for the unstable fluid are generally higher than this value, indicating a greater tendency toward this type of corrosion.

CONCLUSION

The discussion of the tests performed and the results of data recorded during these tests have shown certain indications of correlation with reported service performance. While the tests which were applied were adapted for use by modifying tests originally intended for other types of materials, the results seem to show that they can be of use in evaluating brake fluids. The corrosion and oxidation stability test, as performed, has shown a higher break down to acid products and a greater potential corrosion in use with a combination of cast iron and aluminum at normal atmospheric pressure for a brake fluid considered unstable in service. The results of the Norma-Hoffman bomb oxidation test for time to break down, the formation of acid products, and metallic corrosion under elevated pressure are not conclusive and it is considered that more experience in testing and subsequent correlation with service performance would be required before any conclusions could be drawn from the accumulated data. The fact that galvanic cell current readings can be made on the fluids after the Norma-Hoffman bomb oxidation test would in itself justify the use of this test. The measurements of the current generated in these cells indicate a greater tendency toward galvanic corrosion in the case of the brake fluid which is considered to be unstable.

It is recommended that further similar tests be performed on other brake fluids to be submitted by the Automotive Chemical Laboratory in order to accumulate data which can be correlated with service performance and to assist in the formulation of brake fluids of satisfactory service characteristics. It is also recommended that some consideration be given to the use of a non-gumming, low pour point, corrosion inhibited mineral oil for use as a brake fluid. The use of synthetic rubber packings would be required with a mineral oil base brake fluid. It is further recommended that better mechanical protection against atmospheric moisture and dust be given, if possible, to the operating ends of wheel brake cylinders in use with brake fluids compounded from vegetable oils or soaps carried by volatile solvents.

TABLE I

NEUTRALIZATION NUMBERS
(Corrosion and Oxidation Stability Test)

Condition	Wagner 21-11	Puritan ES-377b
Original	0.09	0.07
After 96 hr. exposure	1.55	3.09
After 192 hr. exposure	6.43	12.4
After 340 hr. exposure	15.0	31.1

TABLE II

CHANGE IN WEIGHT OF METAL TEST PIECES
(Corrosion and Oxidation Stability Test)
IN MILLIGRAMS PER SQUARE INCH
(total at end of each period)

Time	Wagner 21-11		Puritan ES-377b	
	Aluminum	Cast Iron	Aluminum	Cast Iron
24 hr.	0.6 Loss	2.0 gain	0.1 Loss	5.7 gain
50 hr.	0.7 "	2.0 "	2.7 "	4.8 "
72 hr.	0.6 "	2.5 "	3.9 "	4.8 "
96 hr.	0.6 "	2.7 "	6.3 "	5.6 "
125 hr.	0.6 "	2.8 "	11.1 "	5.9 "
192 hr.	0.6 "	3.1 "	36.0 "	6.2 "
288 hr.	0.6 "	2.7 "	87.6 "	5.9 "
316 hr.	0.7 "	2.6 "	not determined	

TABLE III

NEUTRALIZATION NUMBERS
(Norma-Hoffman bomb oxidation test)

Condition	Wagner 21-11	Puritan ES-377b
Original	0.09	0.07
Without catalyst	35.4 at 313 hrs.	9.7 at 518 hrs.
	35.0 at 241 hrs.	9.3 at 518 hrs.
With Aluminum catalyst	27.4 at 217 hrs.	8.3 at 518 hrs.
	31.1 at 217 hrs.	8.3 at 518 hrs.
With cast iron catalyst	31.2 at 345 hrs.	8.3 at 518 hrs.
	10.4 at 361 hrs.	9.0 at 518 hrs.
With Al. and cast iron catalysts	11.4 at 361 hrs.	8.3 at 518 hrs.
	14.4 at 361 hrs.	8.2 at 518 hrs.

TABLE IV

Change in Weight of Metal Pieces used as Catalysts
(Norma-Hoffman Bomb Oxidation Test)
in milligrams per square inch
(total at end of test)

Fluid	Metal	Amount
Wagner 21-11	Al.	0.2 Loss
"	Al.	0.6 Loss
"	cast iron	0.6 Loss
"	cast iron	5.2 gain
"	Al. (with iron in bomb)	0.0
"	Al. (with iron in bomb)	0.4 gain
"	cast iron (with Al. in bomb)	4.7 gain
"	cast iron (with Al. in bomb)	5.9 gain
Puritan ES-377b	Al.	1.0 loss
"	Al.	1.3 loss
"	cast iron	4.3 gain
"	cast iron	7.4 gain
"	Al. (with iron in bomb)	1.1 loss
"	Al. (with iron in bomb)	1.9 loss
"	cast iron (with Al. in bomb)	4.5 gain
"	cast iron (with Al. in bomb)	8.9 gain

TABLE V

Galvanic Current from cells composed of Aluminum and Cast Iron*
Electrodes in Hydraulic Brake Fluid
(in Microamperes per square inch)

Fluid Resistance	Wagner 21-11		Puritan ES-377b	
	one ohm	one hundred ohms	one ohm	one hundred ohms
Time				
41 seconds	4.5	—	—	—
77 "	3.	—	—	—
90 "	—	1.5	—	—
3½ minutes	—	1.0	—	—
8½ "	0.	—	—	—
10 "	—	.4	—	—
12 "	0.	—	—	—
42 "	—	—	—	2.8
50 "	—	—	0.	—
56 "	—	—	—	3.1
21 hours	0.	0.0	0.	6.7
7 days	0.	0.0	0.	3.5
10 "	0.	0.0	0.	2.9
40 "	0.	0.0	0.	2.1
62 "	0.	0.0	0.	2.7

* The cast iron was the positive electrode (cathode) in these tests

TABLE VI

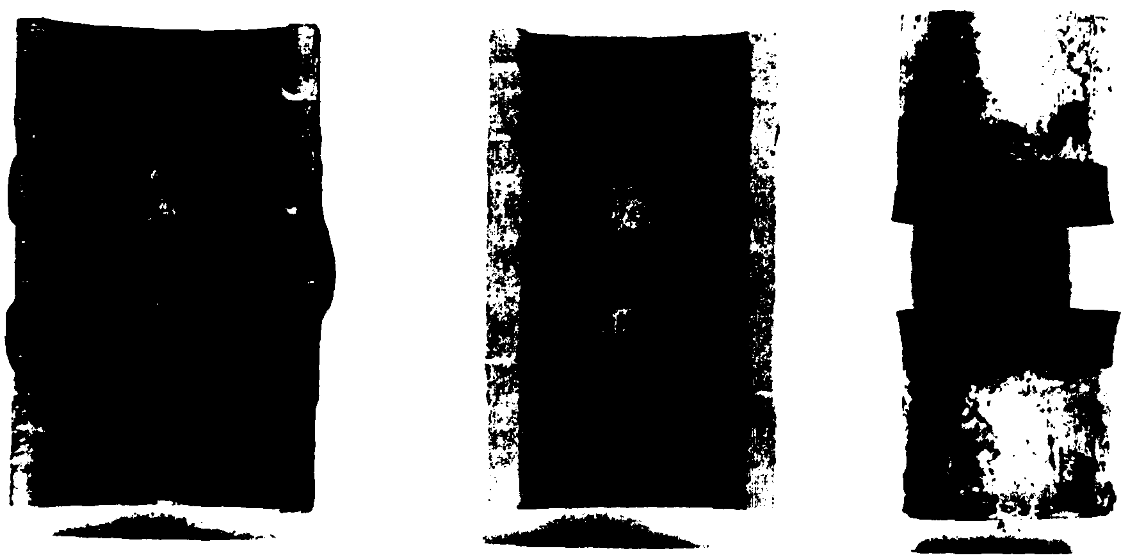
GALVANIC CURRENT IN MICROAMPERES PER SQUARE INCH FROM CELLS COMPOSED OF ALUMINUM AND CAST IRON ELECTRODES IN HYDRAULIC BRAKE FLUIDS FROM THE NORMA-HOFFMAN OXIDATION TEST

FLUID	WAGNER 21-11				PURITAN ES-377b *			
CATALYST*	None	Aluminum	Cast Iron	Aluminum and Cast Iron	None	Cast Iron	Aluminum	Aluminum and Cast Iron
TIME, HRS.								
Up to 1/4	28 -21	-10 11	- -	- -	- -	- -	- -	- -
Up to 1/2	- -	- -	5 0	5 4	28 9	- -	- -	- -
Up to 3/4	- -	- -	- -	- -	- -	8 20	10 6	12 13
3	4 5	3 -11	1 4	2 0	-9 -4	-6 -10	-3 0	16 -12
24	1 0	0 -3	2 0	1 0	-6 -9	-5 -7	-4 -5	-7 -11
47	3 1	1 -3	6 0	2 0	-10 -7	-7 -8	-5 -4	-11 -18
78	-5 -2	-2 -2	-8 0	3 0	-11 -10	-9 -10	-6 -6	-13 -20
240	-8 -5	-2 -2	-13 -3	-1 -1	-5 -6	-4 -5	-4 -2	-8 -11
335	-8 -5	0 0	0 -3	0 -3	-6 -5	-6 -4	-1 0	-10 -13
357	-7 -2	0 0	0 -4	-3 -2	-5 -5	-5 -7	-4 -3	-9 -14

*Catalyst used in the Norma-Hoffman test.

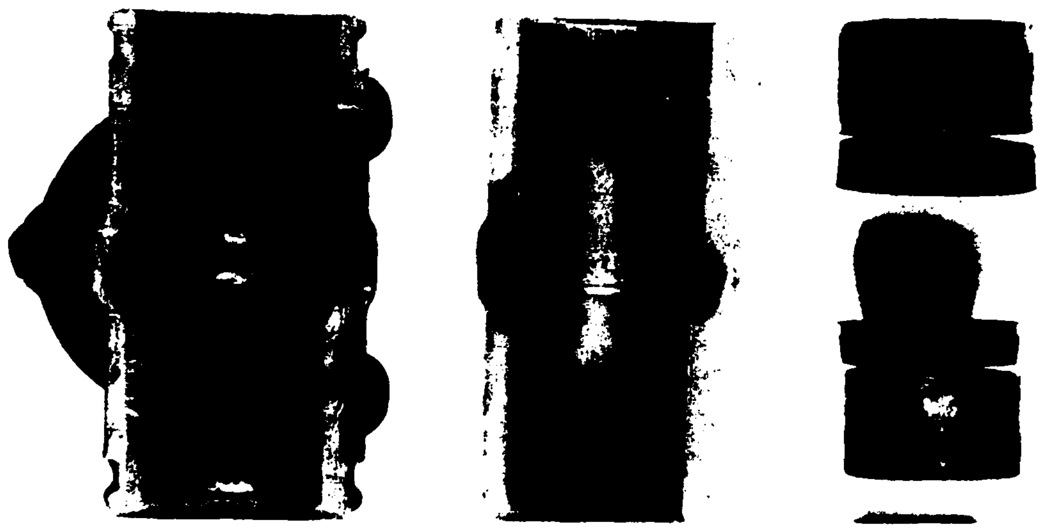
The cell discharged through a one ohm resistance.

The cast iron is the positive electrode (cathode), except when a reversal has taken place, then a minus sign before the figure indicates that the aluminum has become the positive electrode (cathode).



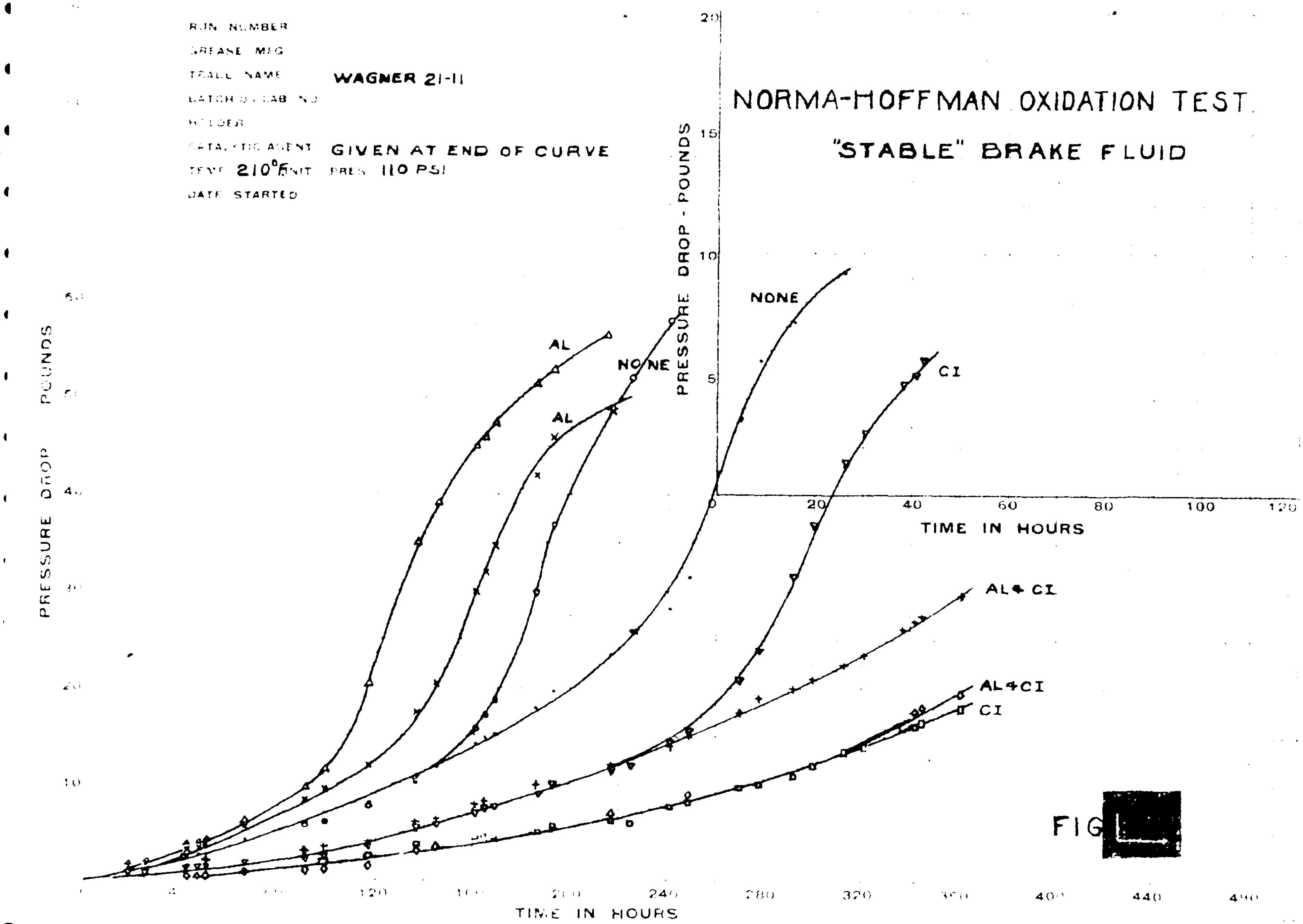
HYDRAULIC BRAKE WHEEL CYLINDER
G.M.C. 6 X 6 2½ TONS LEFT REAR 4391245
19 MAR 1947 WTN.720-775

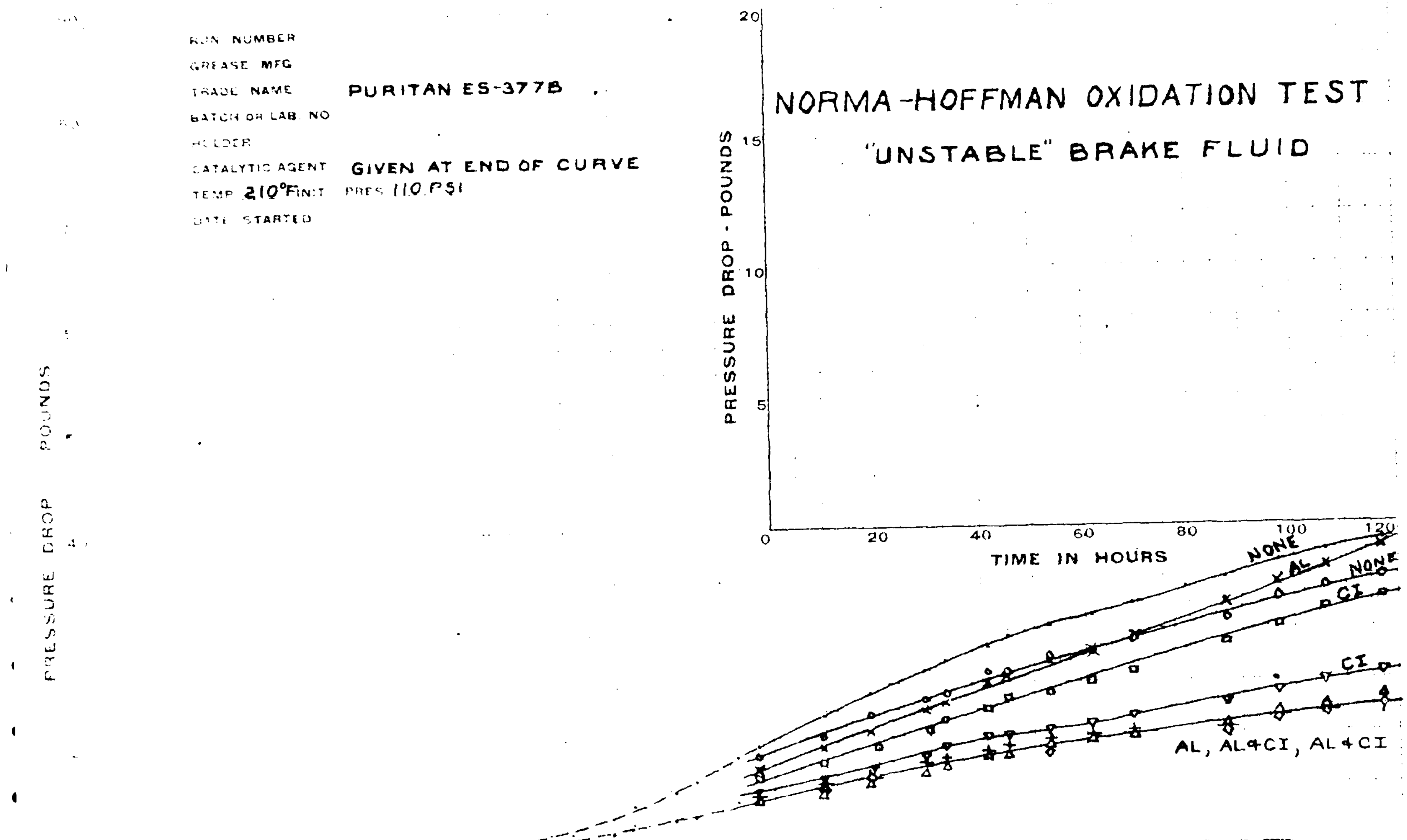
FIGURE 1



HYDRAULIC BRAKE WHEEL CYLINDER
DODGE 6 X 6 $1\frac{1}{2}$ TONS LEFT REAR 32991846
19 MAR 1947 WTN.720-776

FIGURE 2


NORMA-HOFFMAN OXIDATION TEST
"STABLE" BRAKE FLUID
RUN NUMBER
GREASE MFG
TRADE NAME WAGNER 21-11
BATCH OR LAB NO
HOLDER
CATALYTIC AGENT GIVEN AT END OF CURVE
TEMP 210°F INIT PRES 110 PSI
DATE STARTED
PRESSURE DROP POUNDS
TIME IN HOURS
120
240
280
320
400
440
AL
AL
NONE
AL+CI
AL+CI
CI
NONE
CI
PRESSURE DROP - POUNDS
TIME IN HOURS
5
10
15
20
20
40
60
80
100
FIG



FIG[redacted]