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Report on

THE STORAGE STABILITY OF AVIATION GASOLINE IN COPPER FLASHED DRUMS

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ABSTRACT

The use of copper coated drums has been proposed for the storage of aviation gasoline. Since it is well known that metallic copper has a very deleterious effect upon the storage stability of gasoline, the effect of copper coating the steel drum is carefully investigated. The effect of the quantity of dissolved copper in gasoline on the induction period of gasoline is measured. The rate of solution of copper into gasoline for copper flash and solid copper is measured with and without various copper deactivators dissolved in the gasoline. It is shown that the copper flash has such a deleterious effect on the storage stability of gasoline that the use of copper flashed drums cannot be recommended.

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INTRODUCTION

A. <u>Authorization</u>

1. This work was authorized by joint conference of 7 February 1944, between representatives of the Bureau of Aeronautics, Bureau of Ships, Bureau of Supplies and Accounts, and the Naval Research Laboratory, and was conducted jointly under Bureau of Ships Project No. BP-10R and Bureau of Aeronautics Project No. ~~92~~ 60/44.

B. <u>Statement of Problem</u>

2. The inner surface of ordinary cold rolled steel drums used in storing aviation gasoline becomes very rusty in use, and this rust sometimes forms a suspension in the gasoline which settles very slowly. The presence of the rust particles in the gasoline is very undesirable as it tends to plug strainers, jets, and other carburetor equipment in the aircraft engine. As one solution to the rust problem, the use of copper coated drums has been proposed. The copper coat is applied by dipping the steel plate in an aqueous solution of a copper salt, and removing the steel plate after a very thin coat of copper is deposited. This copper plate (or "flash"), in some cases, apparently solves the rust problem, but the presence of copper in contact with gasoline introduces other complications. Copper metal or dissolved copper salts in gasoline have been known for a long time to have a very deleterious effect on the storage stability of any gasoline. The proposition of copper containers for aviation gasoline is studied in order to determine the effect of copper flash on the storage stability of the aviation gasoline.

C. <u>Known Facts Bearing on the Problem</u>

3. There are a number of reports in the literature on the effect of copper in solution in gasoline (1)(2). Copper has been studied in particular because it is the most deleterious of all metals. Also copper and bronze parts are frequently used in gasoline engines. Certain refining operations, such as the Perco sweetening process, frequently leave small quantities of copper in gasoline. It should be emphasized that the studies on the effect of copper in gasoline which have been recorded in the literature point out most strongly the very bad effect of copper in contact with or dissolved in gasoline. It has been demonstrated that 0.1 part per million of copper in gasoline results in a 50% reduction of the ASTM induction period (6). It also is shown that in the presence of one part per million of copper in gasoline, 2 to 5 times the inhibitor concentration (depending upon the inhibitor used) is required to restore the original induction period (1). There are a number of patents on the use of copper supression agents, for example see reference (3). These compounds (called metal deactivators) form stable addition compounds with copper and nulify the accelerating effect of the copper on gumming tendency and lead precipitation.

4. Simpson, Apgar, and Rogers (7) developed a procedure for evaluating metal deactivators. To carry out their test, and 18" length of copper wire, freshly cleaned, was placed in the liner of the ASTM oxidation bomb. A

regular oxidation test is conducted and the induction period is measured by the first appearance of the two pound pressure drop. The deactivator is added to the gasoline in such quantity as to restore the induction period to the original value. The minimum quantity of metal deactivator required to bring the induction period back to that of the original gasoline is a measure of and evaluates the deactivator efficiency.

D. Theoretical Considerations

5. Gasolines, with or without deactivators, may have a very corrosive effect on copper particularly if the fuel is inherently unstable. The two processes of copper corrosion or solution in gasoline and hydrocarbon oxidation accelerate each other. As the copper is dissolved in gasoline, it promotes peroxide formation which decompose to yield other oxygenated bodies including organic acids. These peroxides and acids attack the copper probably following the mechanisms proposed by Denison(5). He has shown that for the corrosion of metals by oil, the peroxides react with the metals to form metal oxides and the oxides are dissolved by the acids formed in the oxidative degredation of the oil. It is shown definitely that the corrosion of engine parts in contact with oil is due to peroxides, and that the organic acids in absence of peroxides are not at all corrosive. It was further shown that corrosion was almost eliminated by the sulfur compounds (naturally occurring in oil) which are oxidized by the peroxides and thus destroy the peroxides.

NARRATIVE OF ORIGINAL WORK DONE AT THE LABORATORY

A. Copper Flash Strips in ASTM Bombs

6. Following the procedure of Apgar, Rogers, and Simpson for testing deactivators described above, a piece of copper flashed iron was found to cut the induction period down to about one-half the value obtained without the copper. A 2" X 1/2" piece of copper foil (.005 inch thick) was tested in the same manner and gave corresponding results. After the induction period had been measured on a strip of copper flashed iron, the strip was examined. It was covered with a heavy, brown, viscous liquid, some of which has collected in the bottom of the glass liner. The copper had disappeared from the surface, as it could not be seen on the used strips after cleaning. It is quite apparent from this experiment that the presence of copper flash has a profound effect upon the gasoline stability.

7. In an effort to measure the effect of metal deactivators on the stability of gasoline in the presence of copper or copper flashed steel, three commercial deactivators were chosen and assigned the following code numbers: D-1, I-1, P-1. (See appendix B for coding system.) The experiments described in paragraph 6 were repeated using varying quantities of D-1 Metal Deactivator dissolved in the gasoline. The results are shown in Table I.

TABLE I

Effect of Metal Deactivator Upon Induction Period

Gasoline	Copper Metal Type	% of Original Ind. Period
Orig. Gas.	Copper Flash	40
Orig. Gas.	Copper Foil	40
+ 1/8 lb. D-1 Metal Deactivator per 5,000 gal.	Copper Flash	50
+ 1/4 lb. D-1	Copper Flash	50
+ 1/2 lb. D-1	Copper Flash	50
+ 1 lb. D-1	Copper Flash	50
+ 2 lb. D-1	Copper Flash	55
+ 4 lb. D-1	Copper Flash	60

As the quantity of deactivator is raised, the induction period is lengthened although not completely restored. The corrosive effect on the copper become less and less, and in the case 4 lbs/5000 gallon of deactivator, the copper surface is clean and unaffected. It is believed, however, that this is much too high a quantity of addend for an aviation gasoline. This direct line of experimentation did not appear to be particularly fruitful, and was not continued.

B. The Relationship between Copper Content & Induction Period

8. In the effect of copper container on gasoline there are two fundamental problems. The first is to prove experimentally the relationship between the quantity of copper in solution in gasoline and the induction period of the gasoline. These data are needed for the quantitative estimation of the effect of copper on gasoline. The second part of the copper problem is to determine the rate of solution of copper into gasoline so that predictions of storage life can be made for the gasoline stored in copper containers.

9. In order to find the relationship between copper content and induction period, a series of copper-containing samples of aviation gasoline were prepared from a well-mixed blend of alkylate, straight run, aromatics, and double pass Houdry gasolines, leaded to 4.3 ml per gallon with Ethyl 1T Aviation Mix. A solution of copper was prepared by dissolving copper tallate* in xylene and adjusting the concentration so that 1.0 ml gives 1 part per million of copper when added to 100.0 ml of the gasoline. Induction period measurements were made upon the gasoline-copper solutions of concentration between zero and 0.4 part per million. The result of this experiment is shown in Plate I. It is concluded from this experiment that as little as 0.1 part per million of copper in gasoline is very dangerous. A report of the Shell Development Company (6) shows this same curve for their gasoline, and this study agrees with theirs closely.

*Copper tallate is the copper salt of "tall" oil, a substance derived from rosin. It was chosen in order to provide a gasoline soluble source of copp

C. Rate of Copper Solution into Gasoline

10. In order to determine how rapidly copper is dissolved by a typical aviation gasoline (in good condition) a sample of gasoline (described in paragraph 9) was placed in contact with fourteen square inches of copper flashed iron, in a glass bottle painted black to keep out light, and allowed to stand in the Laboratory. The concentration of each metal deactivator is 1 lb/5,000 gal., based upon active ingredients. In one bottle was placed an equal area of copper foil .005" thick. Samples of each gasoline were analyzed for copper once a week and the results are shown in Plate II.

11. It may be concluded from this graph that the presence of any of the deactivators increases the rate of solution of the copper in the gasoline. The increase in the rate of solution of the copper is, in the cases of D-1 and P-1 deactivators, very high. The rate of solution is measured from the graph (Plate II), assuming that the rate stays the same as it is in the last 4 weeks of each mesurement, and is shown in Table II.

TABLE II

Gasoline Sample	Rate
1. No Deactivator	0.10 ppm copper per month
2. I-1 Metal Deactivator	0.16 ppm copper per month
3. P-1 Metal Deactivator	0.44 ppm copper per month
4. D-1 Metal Deactivator	0.80 ppm copper per month

The values shown in Table II are very important for calculations of storage life of gasoline in contact with copper and will be referred to later. Since the D-1 Deactivator gives such high rate of solution, its use is not recommended. This same experiment was repeated using the Standard Oil Company of California aviation gasoline which was sent to NRL March 1944 as part of the copper flash problem. The gasoline was taken from the drum marked "cold roll". It has an induction period of about 30 hours. The I-1 Deactivator and the D-1 Metal Deactivator were weighed into xylene and then the proper alliquot was added to the gasoline. The area of copper foil and copper flash is in the proportion as is found in a 50 gallon steel drum, excluding the top. Again, the concentration of deactivator is 1 lb/5000 gal. based upon active ingredients. The samples were allowed to stand in a constant temperature room at 25° C. Results are shown in Plate III.

12. The conclusions to be drawn from the graph of the data, Plate III, are that D-1 deactivator gives a very high rate of solution of copper (as noted above). In case of I-1 deactivator the rate of solution of copper in gasoline is only a little more than that of the gasoline free of deactivator. It is obvious that the rate of solution from the copper flash is much higher than it is from the copper foil. This is due to the spongy nature of the copper flash which exposes a large surface area for reaction.

In the case of the copper foil, there is very little difference in the deactivators, and the rate of solution of copper is not appreciably greater than that of the deactivator free gasoline. Thus any of the deactivators studied would be suitable for use in protecting gasoline which is in contact with copper parts of an engine. It is pointed out that due to this higher rate of solution of the copper into the gasoline, the copper flash will give considerably more trouble than has been experienced from gasoline in contact with copper engine parts.

D. Efficiency of Copper Deactivators

13. The efficiency of the copper deactivators is compared by measuring the induction period of gasoline containing a fixed quantity of copper (1.0 part per million) and inhibitor (1/4 lb/5000 gallons U.O.P. #4) while the quantity of metal deactivator is varied. The curves obtained from these induction periods are shown in Plates IV, V, and VI which are for I-1, P-1, are D-1 Metal Deactivators, respectively. The quantity of deactivator which just restores the induction period to the original 10 hours is the minimum quantity of deactivator required for this particular concentration of copper. The minimum quantity of metal deactivator required (based on active ingredient) to counteract the effect of 1.0 part per million of copper is shown in Table III below:

TABLE III

Deactivator	Quantity Required
I-1	.24 lb/5000 gallon
P-1	.10 lb
D-1	.20 lb

It is apparent from this data that the P-1 deactivator is the most effici However, this deactivator has one very undesirable effect. The copper flashed iron which was placed in contact with this deactivator for twelve weeks showed marked deterioration. (Experiment described in paragraphs 1 and 11.) The film of copper flash changed into a light green powder whic is easily removed from the surface and forms a suspension in the gasoline The other two deactivators left the copper surface clean and bright after a similar period of contact. For this reason the P-1 metal deactivator i not considered further. It is interesting to note from Plate V that the P-1 metal deactivator has strong lead inhibiting power. The study of the I-1 metal deactivator was extended to 2 and 5 parts per million of copper The results are shown on Plates VIII and IX. Assuming that the quantity of deactivator required to restore the induction period to 10 hours is th most desirable quantity of deactivator to have, this required quantity of deactivator is taken from the data on Plates IV, VII, and VIII, and shown on Plate IX. The intersection of the line at 0.1 lb/5000 gallon indicate that there must be present at least 0.1 lb/5000 gallon of the deactivator to be effective.

ESTIMATE OF GASOLINE STABILITY IN COPPER FLASHED DRUMS

A. No Deactivators

14. Estimating the stability of gasoline is a very difficult and somewhat uncertain problem at best. The presence of copper flash complicates the stability estimate greatly for two reasons: (1) the copper is slowly dissolving from the surface and thus the concentration is continually changing; (2) it is not certain that all gasolines react in the same manner as those reported on herein. The data on Plate I indicates that 0.1 part of copper per million reduces the induction period to 50% of what it would be without the copper. Four tenths of a part per million of copper reduces the induction period to 30% of what it is without the copper. From Plate II the rate of copper solution in gasoline is 0.10 ppm per month and thus in 4 months enough copper would have dissolved (under these conditions of temperature) to reduce the stability to 30% of the original. The rate of solution presumably will be much higher under conditions of tropical storage, and the stability consequently greatly lessened. If the gasoline is stable for two years, in steel drums, it appears to be stable for 7 or 8 months in copper drums in temperate climate. Tropical storage would be more severe and the gasoline would be stable for a shorter period, possibly only 4 months. In view of these considerations the use of the copper coated steel drums cannot be recommended as containers for gasoline free of metal deactivators.

B. Using Deactivators

15. If it is acceptable to use metal deactivators in gasoline to be stored in copper flashed drums, the storage stability can be greatly improved. From Table II, paragraph 13, it is observed that the I-1 deactivator shows a 0.16 parts per million copper per month rate of solution from copper flash. If 0.25 lb. per 5000 gal. gasoline of deactivator is used, the copper would have no deleterious effect until after reaching the concentration of 1.0 part per million which would require approximately 5 months; the gasoline would be stable for an additional 6 months, while copper is being dissolved. If 0.5 lb. metal deactivator is used in the gasoline it would counteract 2.0 parts per million Cu and thus the gasoline would be stable for 18 months. On the same basis the 1.0 lbs/5000 gal of metal deactivator would stabilize the gasoline for two years with a certain margin. This calculation is assuming temperate zone storage temperatures. It is probable that the gasoline with maximum quantity of deactivator would not be stable for over one year when stored in tropical regions.

C. Data on Actual Storage in Copper Flashed Drums

16. When the Bureau of Supplies and Accounts first undertook study of this problem, a number of typical fuel drums, including several copper flash drums were constructed and supplied to the Standard Oil Company of California who filled the drums with a 100 octane gasoline from their regular production. The drums were stored outside (40-60° F.) for approximately six weeks when some of them were shipped to NRL in March 1944. The spring and

summer weather of the vicinity of Washington D.C., is the first high temperature to which the gasoline has been subjected. Copper analysis and induction period have been run upon the gasoline at intervals, and the data is shown in Table III.

TABLE III

Date	Copper Content	Date	Induction Period
April 17, 1944	0.01	April 11, 1944	30 hours
May 29, 1944	0.08	----	----
June 26, 1944	0.22	June 25, 1944	8 hours

The gasoline from the cold roll steel drum (filled at the same time as the copper flash drum with the gasoline from the same tank) has an induction period (26 June 1944) of 30 hours. It is evident that the gasoline in the copper flashed drum is deteriorating rapidly and shortly may be expected to fail to pass the 5 hour accelerated gum test. It is also obvious that in hot weather the rate of copper solution into gasoline is much more rapid than in the cool weather; this indicates that tropical storage of gasoline in copper flash drums is not practical.

REFERENCES

(1) Downing, Oil and Gas J 38 #11, 97-101 (1939).

(2) Schildwachter, Kraftstoff 77 117 (1941) CA 38, 1861.

(3) U.S.P. 2, 282, 936, CA 36, 7296.

(4) Grindin CA 33, 2094.

(5) Denison Ind & Eng Chem 36, 477 (1944)

(6) Confidential Report Shell #S-1195 By E. L. Walters.

(7) Apgar, Simpson, Rogers: Report of CRC Gasoline Additives Committee Meeting in New York on December 6-9, 1943, in letter, Shell Oil Co., December 18, 1943, signed M.P.L.Love

Appendix A

METHOD OF COPPER ANALYSIS IN GASOLINE

This method for copper analysis in gasoline is adopted from U.O.P. Method #H-144-40 and modified for use with a colorimeter. Several important refinements are added.

The method essentially consists in reacting an ammoniacal solution of copper with sodium diethyl dithiocarbamate to produce a yellow color the intensity of which is measured in a colorimeter. The steps in the process consist in shaking the gasoline with 4N hydrochloric acid to extract the copper; make ammoniacal and extract yellow color with amyl alcohol; add to alcoholic solution of reagent and react to yellow complex. Measure color intensity in Cenco photolometer using purple filter. The Plate X shows the standard Copper color curve prepared from known copper solutions.

<u>The Procedure for Copper Analysis in Gasoline</u>

1. Measure out 100.0 cc of gasoline and 20.0 cc 4N hydrochloric acid and shake for 10 minutes at about 200 cycles per minute.

2. Take 10.0 cc of acid extract from step 1 and add thereto 8.0 cc 28% ammonium hydroxide solution; shake.

3. Add 10.0 cc of t-amyl alcohol and shake three minutes at 200 cycles per minute.

4. Take 10.0 cc of the lower (aqueous) layer and add 10.0 cc t-amyl alcohol and shake for three minutes. This step removes any residual yellow or brown color.

5. Add 1.0 G of sodium diethyl dithiocarbonate to one liter of water. Add 1.0 cc of this solution to 5.0 cc of 95% ethyl alcohol.

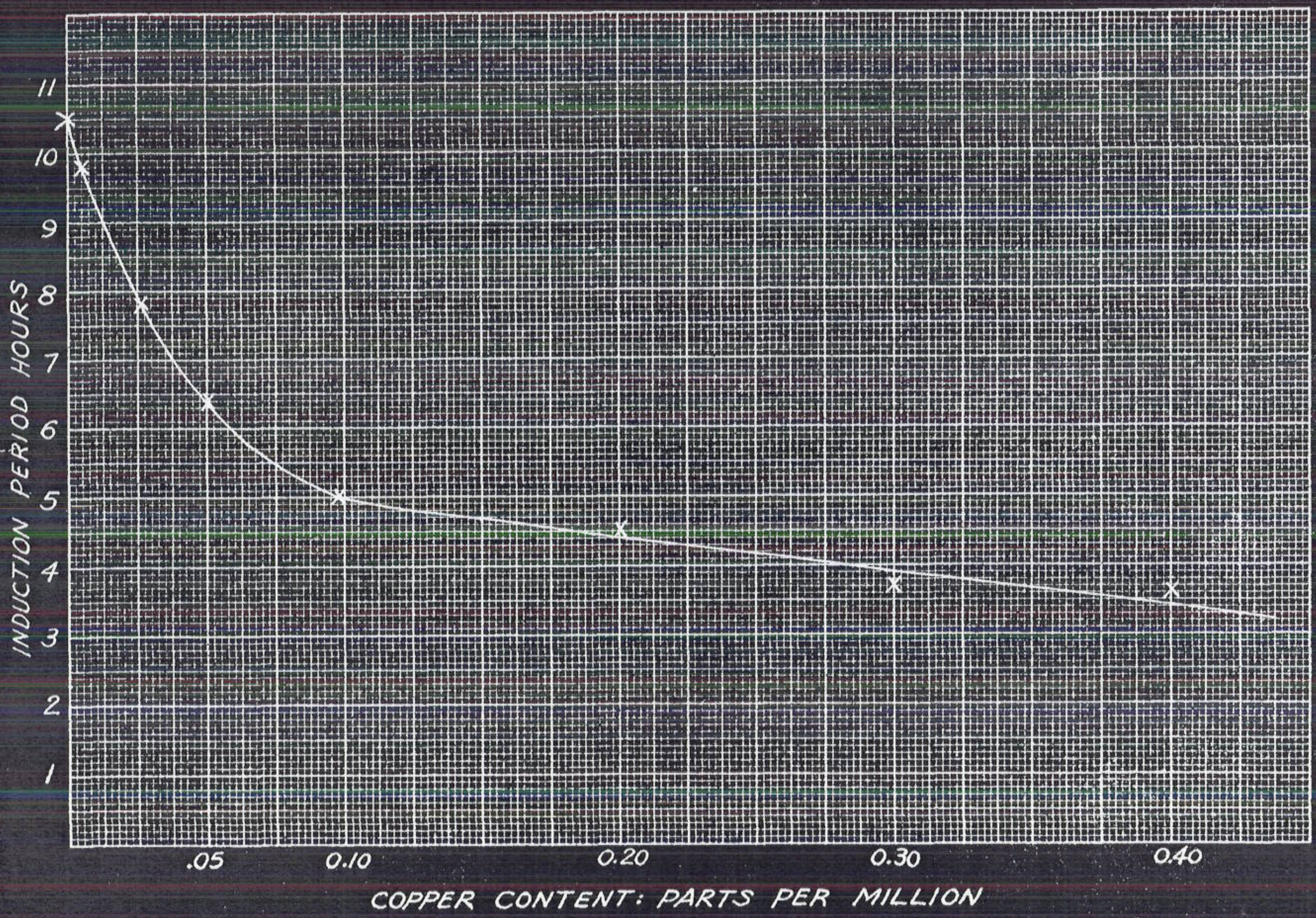
6. Add 5.0 cc of aqueous solution from step 4 to the alcoholic solution of step 5. If copper is present, the solution turns yellow.

7. The intensity of the color is measured with the photolometer using Cenco purple filter #87309A. The concentration of copper is calculated using Plate X, and dividing the result by 5 since 5 times as much gasoline is used as 4N hydrochloric acid.

Appendix B

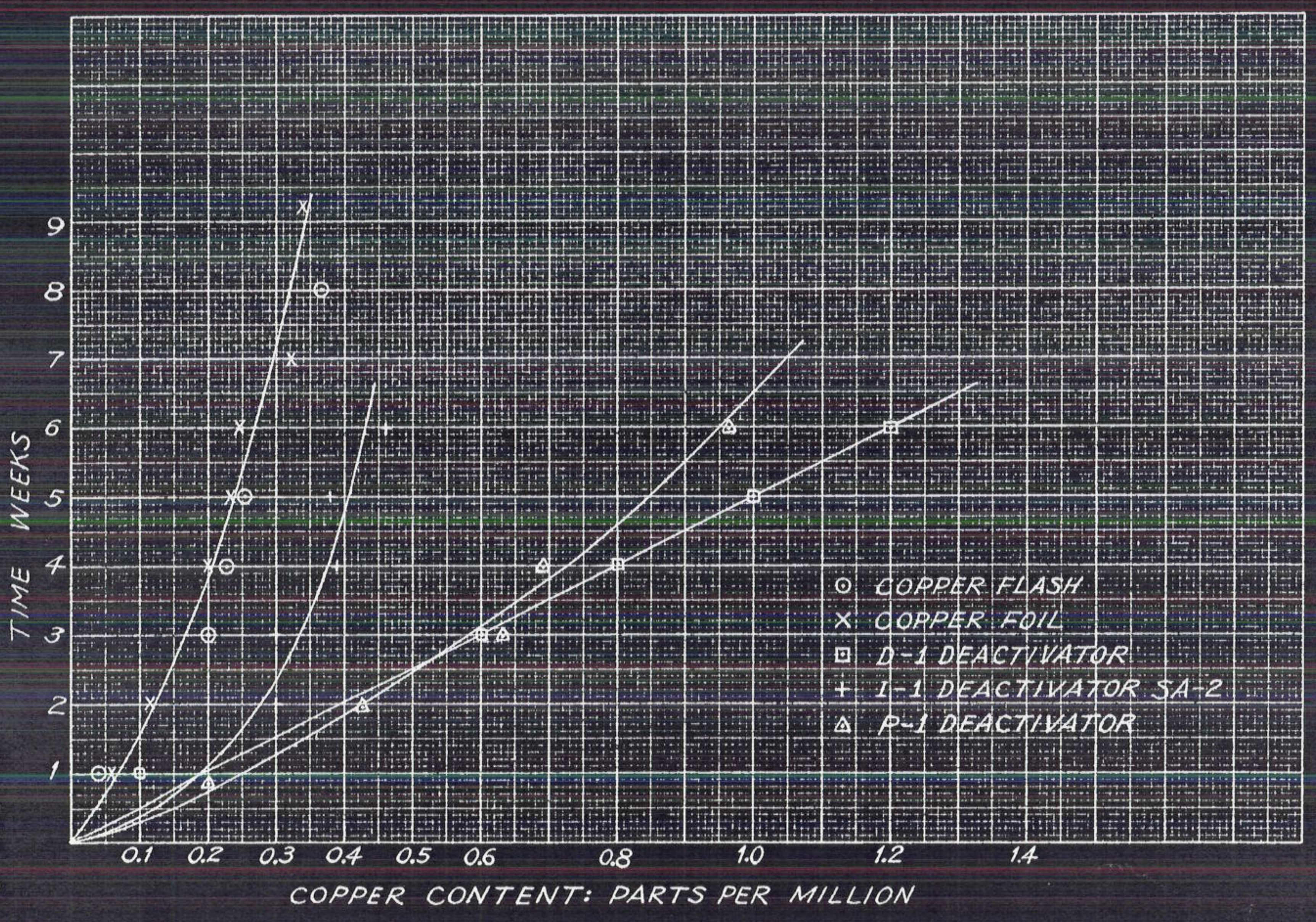
Code System for Metal Deactivators Studied In NRL Report No. P-2329.

Code Number:	Commercial Designation:
D-1	duPont Metal Deactivator
I-1	Standard Oil (Indiana) Deactivator (SA-2)
P-1	U.O.P. Metal Deactivator



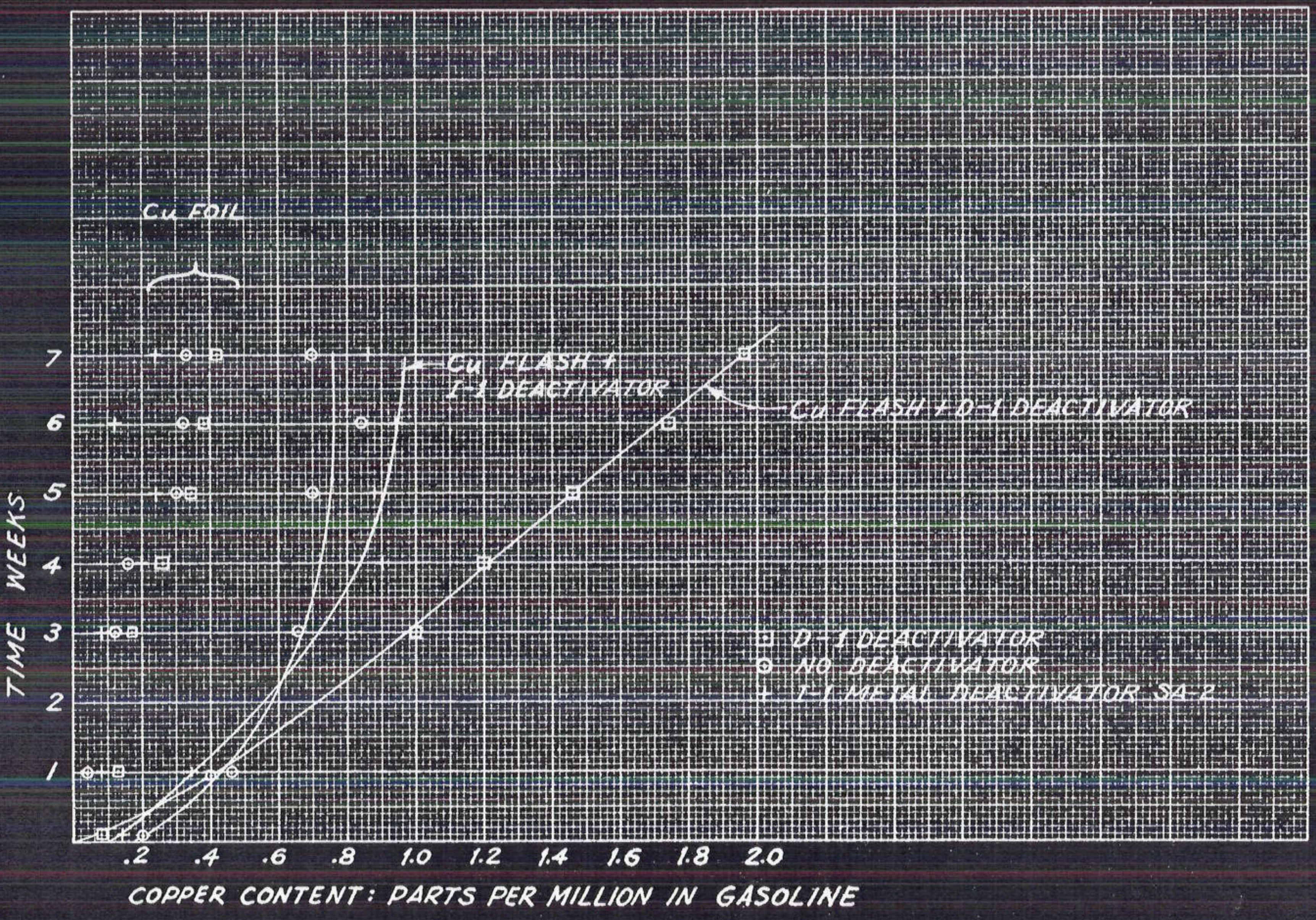
INDUCTION PERIOD HOURS
11
10
9
8
7
6
5
4
3
2
1
.05
0.10
0.20
0.30
0.40
COPPER CONTENT: PARTS PER MILLION

PLATE 1



TIME WEEKS
COPPER CONTENT: PARTS PER MILLION
COPPER FLASH
COPPER FOIL
D-1 DEACTIVATOR
I-1 DEACTIVATOR SA-2
P-1 DEACTIVATOR

PLATE 2



Cu FOIL
Cu FLASH + I-1 DEACTIVATOR
Cu FLASH + D-1 DEACTIVATOR
D-1 DEACTIVATOR
NO DEACTIVATOR
I-1 METAL DEACTIVATOR SA-2
TIME WEEKS
1
2
3
4
5
6
7
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
COPPER CONTENT: PARTS PER MILLION IN GASOLINE

PLATE 3

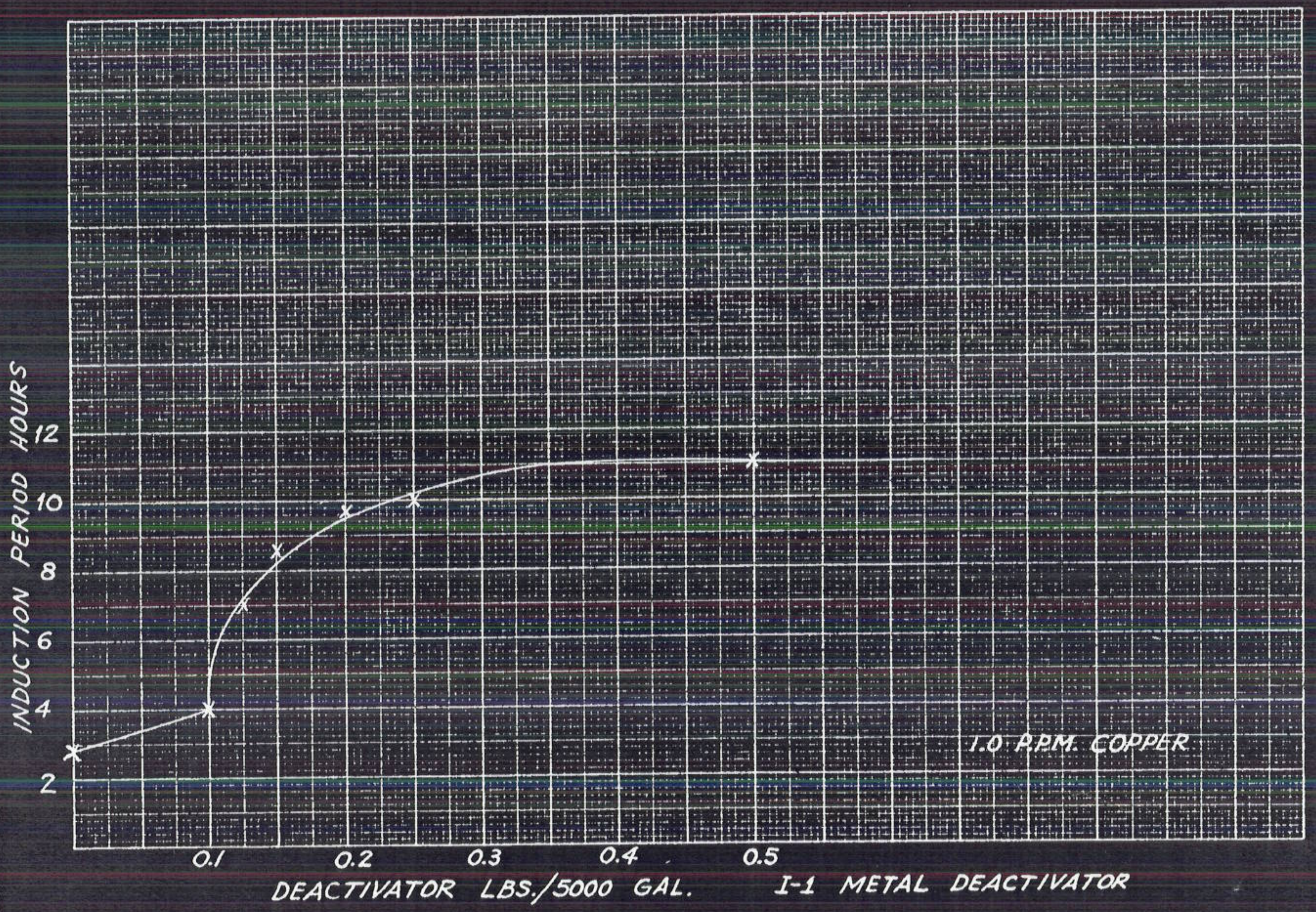

INDUCTION PERIOD HOURS
12
10
8
6
4
2
0.1
0.2
0.3
0.4
0.5
DEACTIVATOR LBS./5000 GAL.
I-1 METAL DEACTIVATOR
1.0 P.P.M. COPPER

PLATE 4

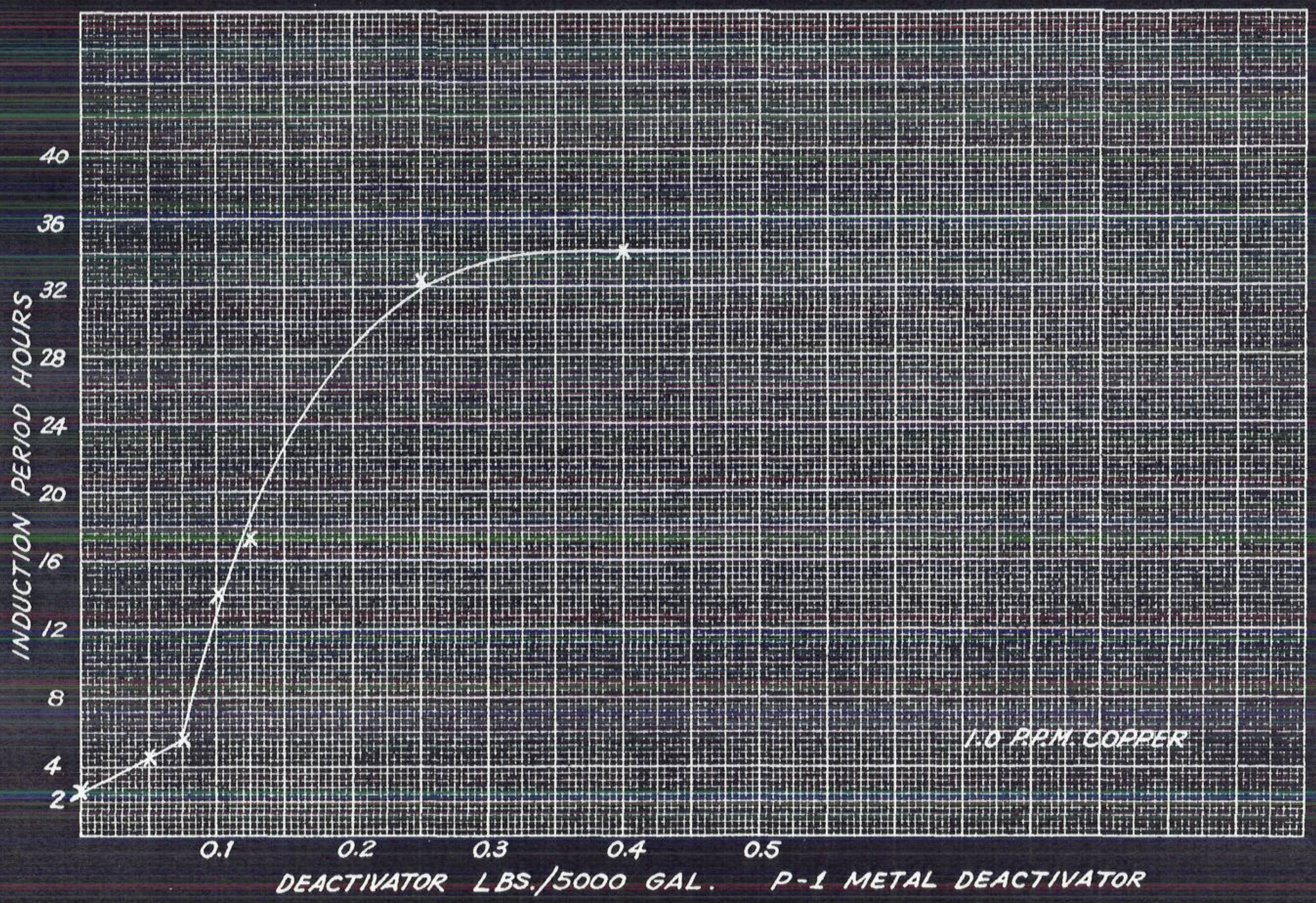
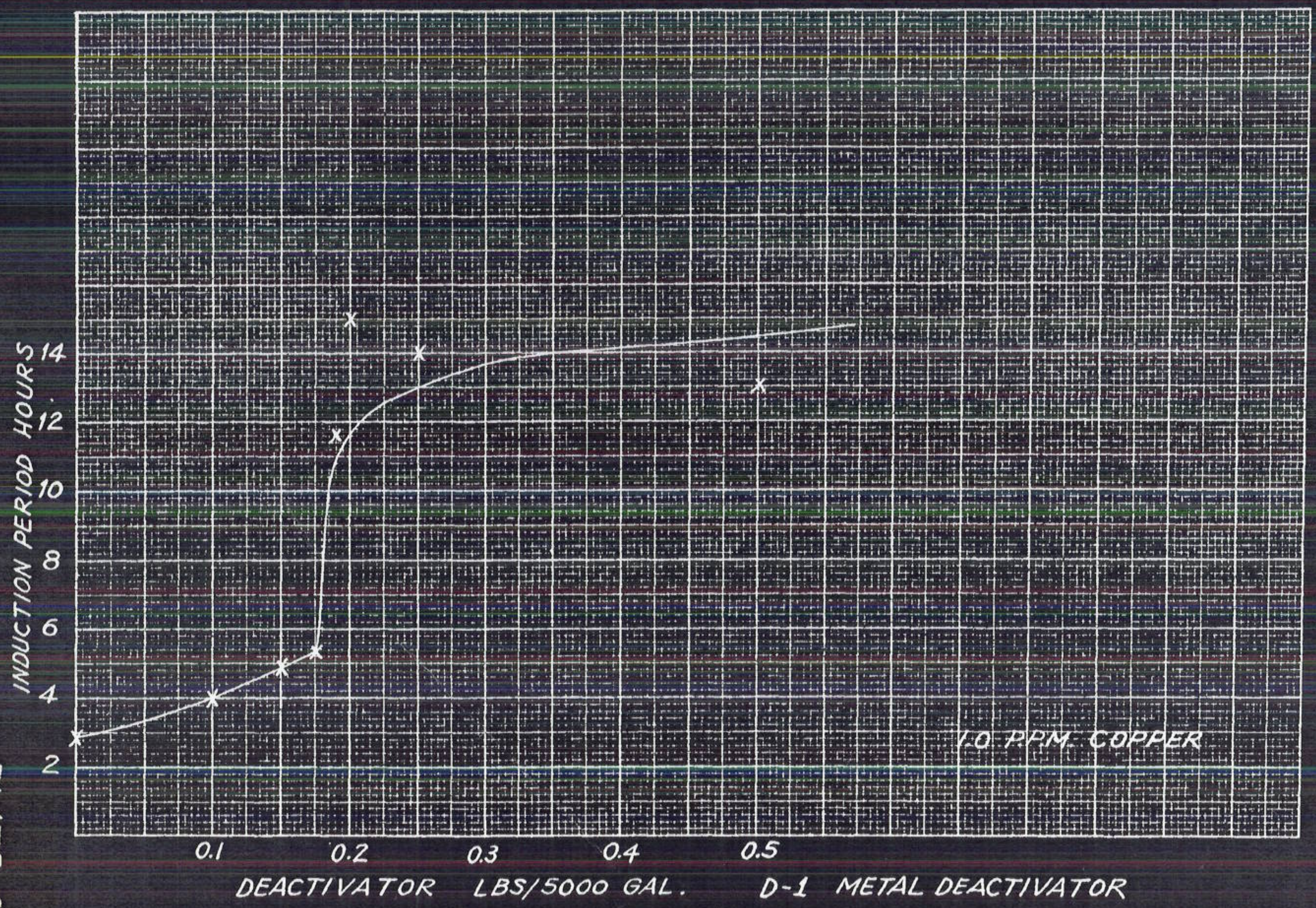

INDUCTION PERIOD HOURS
40
36
32
28
24
20
16
12
8
4
2
0.1
0.2
0.3
0.4
0.5
DEACTIVATOR LBS./5000 GAL.
P-1 METAL DEACTIVATOR
1.0 P.P.M. COPPER

PLATE 5



INDUCTION PERIOD HOURS
14
12
10
8
6
4
2
0.1
0.2
0.3
0.4
0.5
DEACTIVATOR LBS/5000 GAL.
D-1 METAL DEACTIVATOR
1.0 PPM. COPPER

PLATE 6