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REPORT NO. 36

E.I. DU PONT DE NEMOURS & CO.
FABRICS AND FINISHES DEPARTMENT
CHEMICAL DIVISION

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Parlin Laboratory

SUBJECT: Gassing of 259 Line "Fuse"

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INTRODUCTION

As a result of periodic complaints pertinent to the development of pressure in containers which package the 259 line "Duco" enamels, a study was made to determine

(a) the cause of gas formation,
(b) the nature of the gas, and
(c) methods of reducing the amount of gassing.

It became a further purpose of this study to establish a control test by which certain constituent materials in "gas producing" lacquers could be evaluated with regard to their tendency to generate gas.

CONCLUSIONS

From the experimental work described herein the following conclusions may be drawn regarding gassing of 259 line "Duco":

(a) The gas produced may be attributed to the inherent gassing of Archer-Daniels-Midland Co. No. 100 Blown Linseed Oil (M-141) used in the formulation of the 259 line (See Figure 3). It may also be noted that in a comparison of three drying oils, namely Archer-Daniels-Midland No. 100 Blown Linseed Oil (M-141), Archer-Daniels-Midland No. CL-200 Blown Soya Bean Oil (M-194), and Baker's M-393 Blown Soya Bean Oil (M-193), the ratio of gas produced by each, under identical conditions, was in the ratio of: 1:0.5:0 respectively.

(b) The gas generated is essentially hydrogen.

(c) The amount of peroxide present in blown linseed oil or blown soya bean oil, or in lacquers containing these oils, is indicative of the tendency of these materials to produce gas (See Curves I and III). Conversely, if any of these oils or lacquers are made to evolve its gas, the resulting material will give no evidence of peroxides (See Curve II). Furthermore the relationship between the amount of gas produced by such materials and the amount of peroxides present in them is directly proportional (Compare Figures 1, 2 and 3 with Curves I, II and III respectively).

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(d) The presence of peroxides in blown linseed or blown soya bean oils, or lacquers made with these oils may be detected by a noticeable rise in temperature, produced when such an oil or lacquer is heated with a small amount of a solution of Cobalt Naphthenate (or Cobalt Linoleate) in mineral spirits.

(e) The amount of gassing in a drying oil may be effectively reduced by

1. refluxing the oil at elevated temperatures (100°-110°C) for a six to eight hour period with provision for allowing the accumulated gas to be released, or

2. aging the oil for longer periods at moderate temperatures (20°-30°C) with periodic venting.

EXPERIMENTAL

The experimental work may be best described in dividing it as follows:

I. Consideration of Containers
II. Test Methods
III. Analysis of Gas
IV. Performance of the Drying Oils
V. Performance of the 25% Line "Duco"

I. Consideration of Containers

At the outset the cause of gassing was believed to be due to gas generated by one or more of the constituents of the 25% line "Duco" or by the reaction of the enamel with the material of construction of the container.

Inasmuch as all of the work regarding the container materials has not been completed, the results of observations will be listed without any attempt to draw conclusions:

(a) Examination of 25% line "Duco" packaged in one gallon lead cans stored at the Perlin Shipping Warehouse showed no evidence of gassing, where the material was recently packaged, but considerable evidence of gassing in containers packaged six to eight months previous to the examination.

(b) Field visits to the New York, New Haven and Hartford Railway Shop at Queens, N.Y. the Lee Finish Corporation, New York City, and the American Air Lines terminal at La Guardia Field, lead to the following conclusions (Re: Letter from R.O. Ieele to Russell Morgan dated 10/22/45):

1. No evidence of gassing in 5 gallon Canco containers (resin coated, black iron sane) even though contents were twelve to twenty months old.

2. Considerable evidence of gassing in one gallon and one quart lead containers.

3. No evidence of gassing in fiber containers.

4. Most severe gassing with red, orange and greens.

II - Description of Principle Test Methods

The methods of testing, observing, and measuring performed in this work included:

(a) Observations of bulging of lead containers upon gassing of the contents.

(b) Measurement of the length of column of gas produced in a fermentation tube where the free space at the start is zero. (Fermentation tubes are shown in Figures 1-3 inclusive).

(c) Orsat Method of gas analysis for carbon monoxide, carbon dioxide, oxygen and hydrogen; nitrogen was determined by difference.

(d) Colorimetric determination of peroxides based on the oxidation of ferrous to ferric iron with the characteristic formation of red ferriferrithiocyanate as described in the Analytical Edition of "Industrial and Engineering Chemistry" for May 1936, pp. 195-199.

(e) Determination of peroxides by use of Cobalt Drier (VD-1450) and measuring temperature rise with time. This test depends on the exothermic reaction which takes place between a peroxide and the solution of Cobalt Naphthenate or Cobalt Linoleate in mineral spirits. The procedure used consists in the addition of 5 cc. of Cobalt Drier (VD-1450) to a 50 gm. sample of oil or lacquer. Notation was made of the temperature at intervals of one minute. The mixture was stirred constantly. Temperature rise vs. time is then plotted.

XII - Analysis of the Gas

Results of Gas Analysis of the gas show the following (ref letter from H. Wade to J.H. Lovell dated 10/30/45):

Carbon Dioxide	1.2%
Unsaturates	0.0
Oxygen	0.7
Hydrogen	74.0
Carbon Monoxide	1.0
Nitrogen (By difference)	23.1

XV. Performance of the Drying Oils

Observations and experimental tests made on the three drying oils, namely K-141, K-196 and K-193 showed

(a) Drums in raw materials storage showed bulging where contents were K-141 or K-196. No bulging of drums of K-193 were evident. Samples were put in gallon cans and subjected to elevated temperatures. These cans likewise bulged where the contents were K-141 and K-196.

(b) Samples of drying oils were placed in fermentation tubes and allowed to age at elevated temperature. The results are indicated in Figure 1. After a period of two weeks at 40°C. K-141, produced 3.5 inches of gas, K-196 produced 2.7 inches of gas and K-193 shows no gas formation.

(c) The effect of heat treatment on K-141 was demonstrated by heating samples for 2-1/2, 5 and 8 hours respectively, and then comparing these samples with an untreated sample, by placing a like quantity of each material in a fermentation tube and subjecting the tubes to 40°C. temperature for a ten day period. It will be noted from Figure 2 that whereas the untreated sample produced 2.7 inches of gas, heating for 2-1/2 hours at 110°C. reduced the amount of gas to 1.6 inches, 5 hrs. heating at 110°C. reduced the amount of gas to 1.0 inches, and 8 hrs. heating at 110°C. reduced the amount of gas to less than 0.5 inches.

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(d) The peroxide content of the three drying oils was compared by noting the temperature rise vs. time upon addition of Cobalt Drier (VM-1450) to each of the oils. Results of these tests are plotted as Curve I and indicate that the ultimate temperature elevations in a twenty-five minute period were in the ratio of 4:3:1 for K-142, K-198 and K-193, respectively.

(e) The effect of heat treatment on K-142 drying oil has been described above in regard to reduced gas formation. Samples of the heated oil were treated with Cobalt Drier (VM-1450) to determine the peroxide content. Results of temperature rise vs. time data are plotted as Curve II. It will be noted that heating results in a decrease in peroxide content. It will also be noted that the decrease in peroxide content of samples receiving the same heat treatment is proportional.

(f) The presence of peroxides in the oils was also determined colorimetrically (as H_2O_2) and the results were found to agree with those obtained by the test method established in this study. The results of the colorimetric method are (re: letter from E. Klein to J.K. Lowell dated 10/29/45):

K-142 (untreated)	0.46%
K-142 (heated slightly)	0.32
K-142 (heated for several hrs.	0.23
K-198	0.21
K-193	0.00

V - Performance of Inhibitor

In order to demonstrate that K-142 was the direct cause of gas formation in 599 line "Dumo" engine a laboratory batch of 599-030 was prepared, omitting the required amount of K-142. To one-half of this batch was presented amount of K-142 was added. Samples of the 599-030 containing K-142 and 599-030 minus K-142 were then placed in fermentation tubes and aged at 120°. After a 10 day period the material containing K-142 produced 0.5 inch of gas, while the sample having no K-142 showed no gassing. See comparison in Figure 3.

A comparison of the peroxide content of a sample of 599-030 containing K-142 was made against a sample of 599-030 minus K-142. The results of these tests, which are shown as Curve III are in complete agreement with the facts that

(a) peroxide content is indicative of tendency to form gas, and

(b) presence of K-142 in 599 line "Dumo" is the chief cause of gas formation.

LC:MCN

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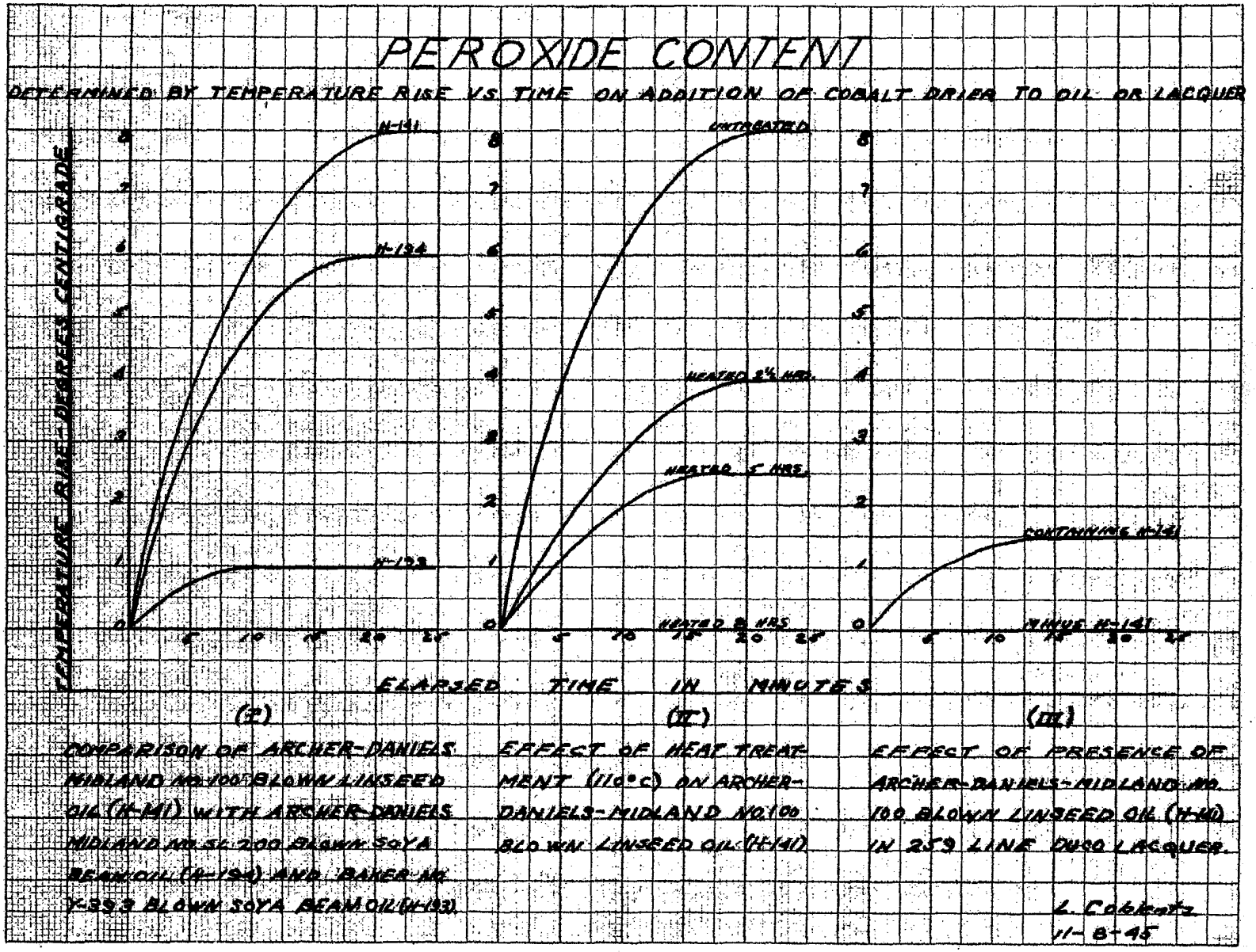

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RELATIVE GASSING IN DRYING

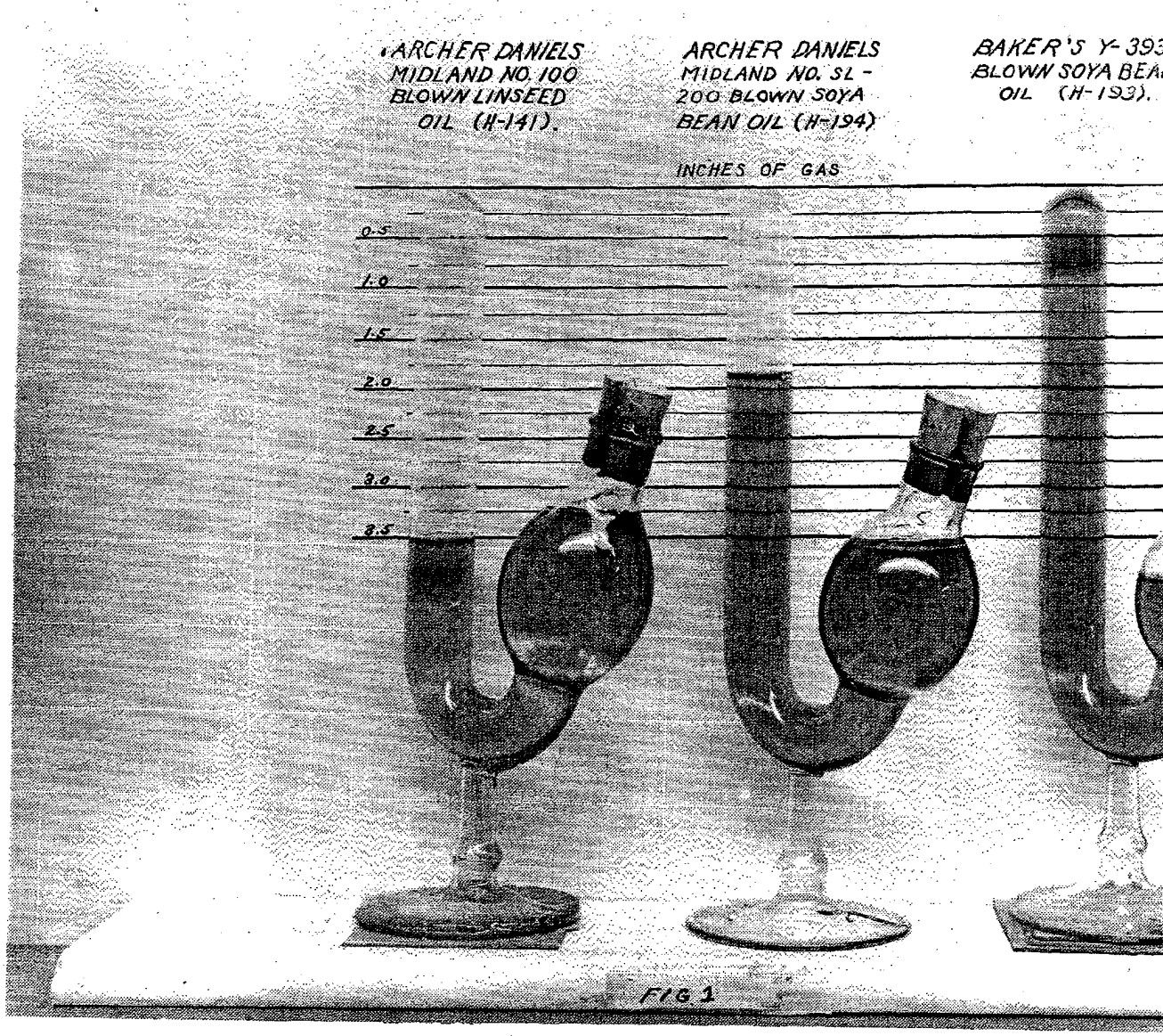

FIG 1

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THE EFFECT OF HEAT TREATMENT ON ARCHER DANIELS MIDLAND NO. 100 BLOWN LINSEED OIL

UNTREATED | HEATED AT 110°C FOR 2½ HOURS | HEATED AT 110°C FOR 5 HOURS | HEATED AT 110°C FOR 8 HOURS

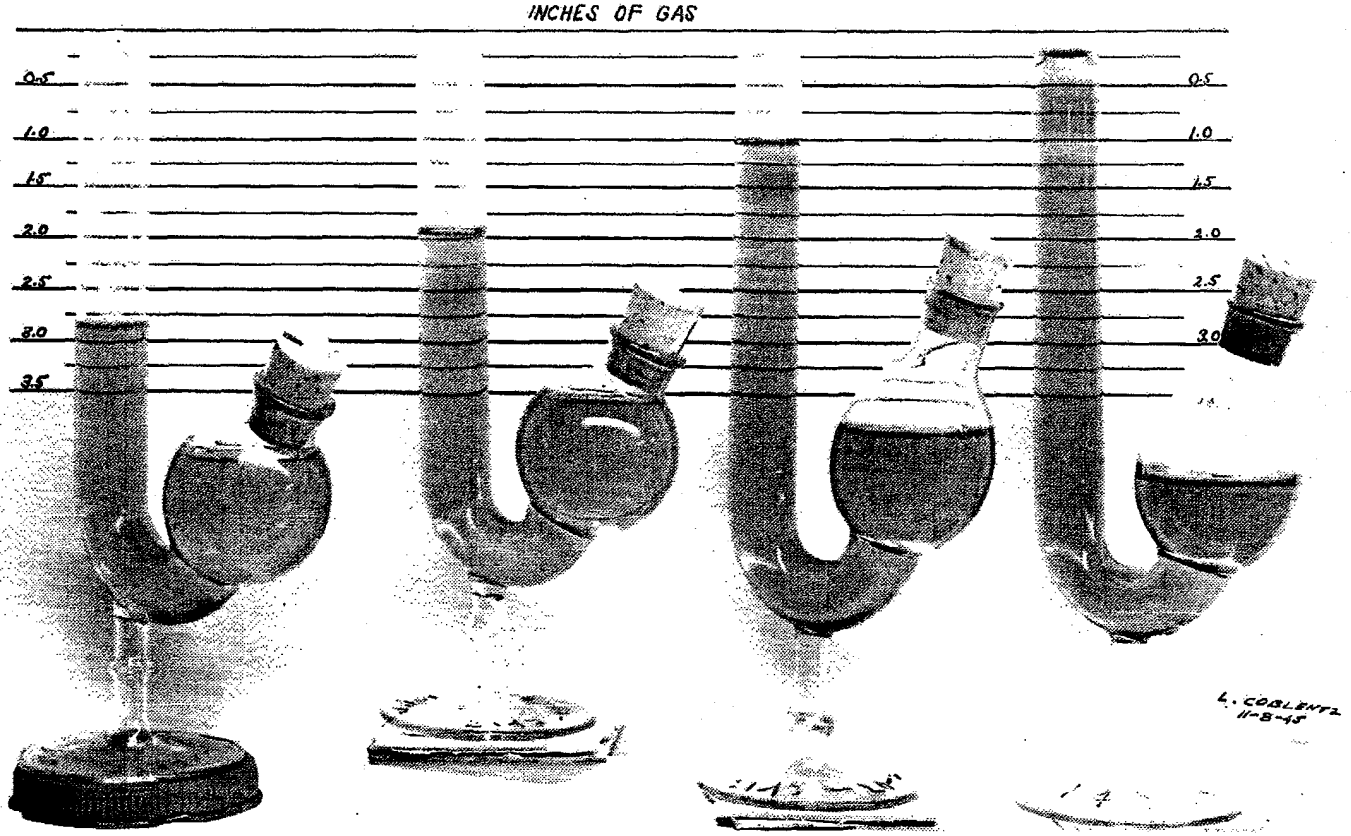

FIG. 2

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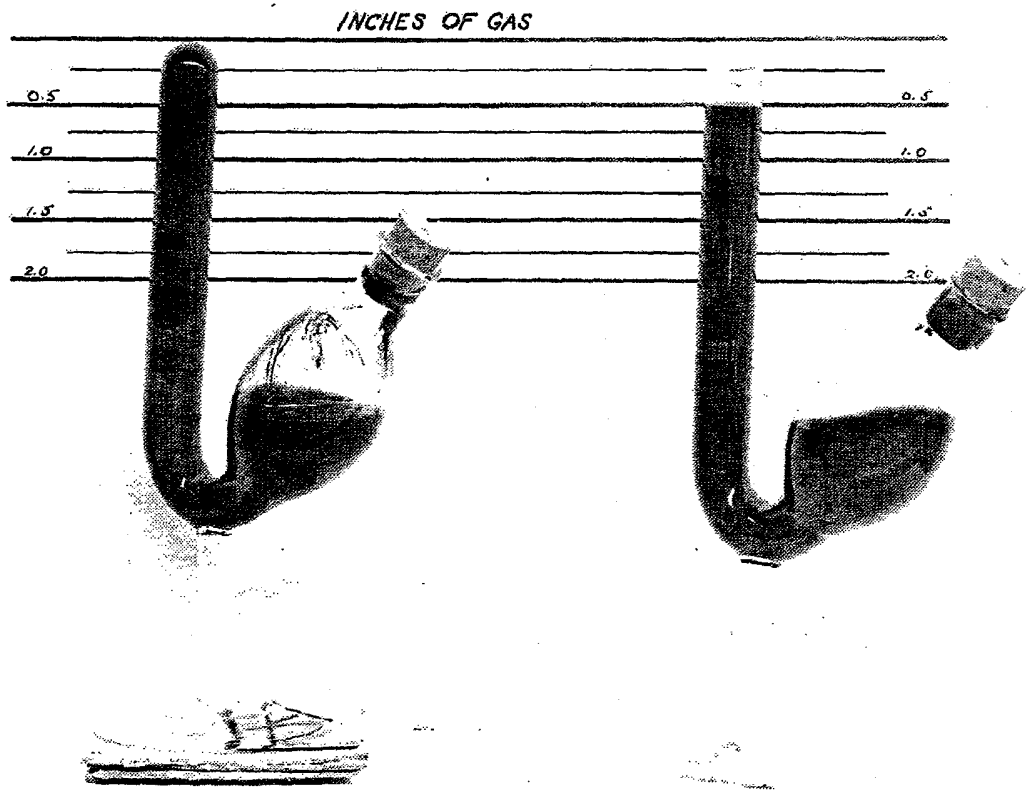
EFFECT OF PRESENCE OF A.B.T. 100 BLOWN LINSEED OIL (H-141) ON GASSING OF 259 LINE DUCO LACQ.

259-030 LACQUER MINUS H-141

259-030 LACQUER CONTAINING H-141



L. COGLENTZ 11-5-45

FIG. 3

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