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Direct Spectrophotometric Determination of Lead Naphthenate in Linseed Oil

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DIRECT SPECTROPHOTOMETRIC DETERMINATION OF LEAD NAPHTHENATE
IN LINSEED OIL

BY
NICHOLAS PETER OEHLBerg

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE
IN LOYOLA UNIVERSITY

DECEMBER
1943
VITA

Nicholas Peter Oehlberg was born in Chicago, Illinois on October 22, 1909.

He graduated from Nicholas Senn High School, Chicago, Illinois in June, 1927.

The Bachelor of Science degree in Chemistry was conferred by Loyola University in June, 1932.

He attended Loyola University, graduate school, studying graduate mathematics from 1932 to 1937.

The past four years were devoted by him to the graduate study of chemistry.
ACKNOWLEDGEMENT

The author expresses his gratitude to his advisor,
Dr. George M. Schmeing, Chairman of the Department of Chemistry of Loyola University for his interest, suggestions and guidance, to Reverend Francis J. Gerst, S. J., Dean of the Graduate School of Loyola University for his helpful criticism and assistance, and to Mr. Al Stresen-Reuter of the Frederick Stresen-Reuter Company of Chicago for supplying chemicals used in this problem.
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Quantitative determination of lead in linseed oil for control is a laborious and time consuming process. This work covers a rapid method for the determination of lead naphthenate in linseed oil that may easily be used in similar determinations.

The original scope of this report was to cover all lead salts and their solutions used as driers for linseed oil. Investigation showed that the spectrophotometer could not be used for determining the percent of lead for all types under the conditions imposed. Hence data were compiled only on lead naphthenate.

The term "drier" means catalyst. Lead and other metal salts and soaps have a catalytic effect on semi-drying and drying oils, producing an oxidized film.

Lead is the first metal\(^1\) to be used as a drier for linseed oil. The function of driers is still a mystery\(^2\) despite the work that has been done. Other metals that perform the function of a drier are cobalt and manganese.

Metals that act as driers are used in the form of oxides, salts, or soaps. Soaps commonly used today are the linoleate and resinate.

In dissolving the oxide the metal soap of the fatty acid present in the oil is formed. The linoleate is made from
a soluble metal salt and the fatty acids of linseed oil. The resinate is produced from a soluble metal salt and rosin reacted with lye.

In solution form beside the linoleate and resinate, metal naphthenate, produced from petroleum, has found favor due to greater solubility.3, 4, 5.

The solution form is usually produced by dissolving the proper soap or naphthenate in a petroleum fraction that is known as mineral spirits or into a special fraction.

At present lead is determined by precipitation as thioglycolate6, as oxalate7 and as sulfate, and electrolytically as oxide PbO2. Jarrett8 has used a semi-colorimetric method in determining cobalt, lead, and manganese, but he did not estimate the lead colorimetrically.

No references were found in the literature on a spectrophotometric determination of lead in linseed oil although this is a rather obvious method for control of the lead concentration.

Materials used in the following study are:

Lead Linoleate (27% lead)
Lead Naphthenate Solution (24% lead)
Lead Linole-resinate Solution (24% lead)

Frederick Stresen-Reuter, Inc. of Chicago, Illinois
Superb Linseed Oil

Procter and Johnson of Chicago, Illinois

Mineral Spirits

Standard Oil of Indiana

In order to determine the possibility of comparison of the three lead salts, solutions containing one percent lead as metal were made in linseed oil and in a mixture composed of fifty percent linseed oil and fifty percent mineral spirits. These solutions were aged six weeks and then examined.

Only lead naphthenate remained dissolved. The linoleate and lino-resinate solutions contained a lead bearing precipitate and were considered useless for further study for the spectrophotometer.

This test proved the value for the lead naphthenate solution and corroborated previous experimental work.

The lino-resinate solution was used in place of the resinate due to claims of greater solubility than the linoleate, but the precipitates were equal in weight.

In considering mineral spirits as the solvent, the fact that it is present in every laboratory handling linseed oil problems is an important one. Further, it has a low rate of evaporation and solutions made with it can be handled without change in concentration. Other solvents can be used but
they have a faster rate of evaporation.

Experimental Procedure

Solutions of lead naphthenate in linseed oil were made containing 0.1, 0.2, 0.5, and 1.0 percent lead (as metal). These solutions were diluted to fifty percent solids by weight with mineral spirits and aged for four weeks as a further check on solubility.

A pair of test tubes was matched using the recommended dichromate method. These were carefully marked and used as holders for the solutions in the instrument.

Transmission of the solutions was measured on the Coleman Universal Spectrophotometer, using the direct reading from the galvonometer scale. The readings were repeated for check.

Readings using the Null method were not successful.

The data covering the solutions using air as reference are in table I, and those using a reference composed of fifty percent linseed oil and fifty percent mineral spirits are in table II.

In all the tests, a PC-4 filter was used. It is recommended for the wavelength range 400 to 700 millimicrons.

An attempt was made to obtain readings below 415
millimicrons by using a deep purple filter PC-6, suggested for operation in the range 350 to 400 millimicrons. No readings were obtained.

Trial readings of the undiluted solutions were also unobtainable, probably due to the color strength of the oil.

No attempt was made to dilute the solutions further. Previous work has indicated partial separation of the various components in greater dilution.

Variations in the instrument readings were finally traced to the storage battery and were controlled by keeping the battery fully charged.

Another variation was traced to the temperature of the solutions. All readings were taken with the solution temperature at 25° Centigrade.

Discussion of data

An examination of the curves in graph 2 shows the greatest slope for the curve plotting log percent of transmission against percent of lead concentration for 400 millimicrons. The curve for 420 millimicrons is also suitable but would not permit as great an accuracy in determining the percent of lead in an unknown as the curve for 400 millimicrons.

Using air as a reference a straight line is not
plotted, indicating that Beer's law does not hold. This type of curve has been reported in the literature for carotene as satisfactory.

Using a reference of fifty percent linseed oil and fifty percent mineral spirits, only one point is obtained for 0.1 percent lead concentration (Table II). It is at 415 millimicrons. Log percent of transmission is plotted against percent of lead concentration for this wavelength in Graph 4. Again the curve shows that Beer's law does not hold.

A comparison of Graph 2 and Graph 4 shows that the air reference method for 400 millimicrons is more accurate than the mixed standard method for 415 millimicrons.

Conclusions

Use of the Coleman Universal Spectrophotometer for the direct determination of lead naphthenate may be considered as a rapid and accurate control method.

The air reference method is recommended over the linseed oil - mineral spirits reference method.

Suggestions for further work

Work could be done with the spectrophotometer using lead naphthenate with other vegetable oils. The determination of cobalt and manganese naphthenates in various oils could be
run and these results correlated to this investigation to determine whether a method for the determination of the three drier metals, cobalt, lead and manganese, could be found.
REFERENCES

1. F. Fritz, Farben Zeitung, 43, 755, 801, 806 (1938)
4. Harkness and Brunn, Industrial and Engineering Chemistry, 32, 499 (1940)
5. "Facts about Nuodex", Nuodex Products Co, Inc., Elizabeth, New Jersey
8. Jarrett, J., Oil and Color Chemists Association, 23, 29 (1940)
### TABLE ONE

**AIR REFERENCE WITH PC-4 FILTER**

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TABLE TWO

50% LINSEED OIL AND 50% MINERAL SPIRITS STANDARD

PC-4 FILTER

PERCENT OF LEAD (AS METAL)

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</tbody>
</table>
LINSEED OIL - MINERAL SPIRITS
REFERENCE
PC-4 FILTER
GRAPH 4
Approval Sheet

The thesis submitted by Mr. Nicholas F. Oehlberg has been read and approved by three members of the Department of Chemistry.

The final copies have been examined by the director of the thesis and the signature which appears below verifies the fact that any necessary changes have been incorporated, and that the thesis is now given final approval with reference to content, form, and mechanical accuracy.

The thesis is therefore accepted in partial fulfillment of the requirements for the Degree of Master of Arts.

Dec. 8, 1943
Date

Signature of Adviser