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MISCELLANEOUS TARGETS

JAPANESE FUELS AND LUBRICANTS - ARTICLE 9
FUNDAMENTAL HYDROCARBON RESEARCH

U.S. NAVAL TECHNICAL MISSION TO JAPAN

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U. S. NAVAL TECHNICAL MISSION TO JAPAN
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SAN FRANCISCO, CALIFORNIA

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From: Chief, Naval Technical Mission to Japan.
To : Chief of Naval Operations.

Subject: Target Report - Japanese Fuels and Lubricants, Article 9 - Fundamental Hydrocarbon Research.

Reference: (a)"Intelligence Targets Japan" (DNI) of 4 Sept. 1945.

1. Subject report, covering miscellaneous Japanese data on the physical properties of some pure hydrocarbons outlined by Targets X-09, X-10, and X-38(N) of Fascicle X-1 of reference (a), is submitted herewith.

2. The investigation of the target and the target report were accomplished by Comdr. G. L. Neely, USNR, Lt. Comdr. C. S. Goddin, USNR, and Lieut. W. H. Millet, USNR, assisted by Ensign E. R. Dalbey, USNR, as interpreter and translator.

C. G. GRIMES
Captain, USN

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SUMMARY

MISCELLANEOUS TARGETS

JAPANESE FUELS AND LUBRICANTS - ARTICLE 9
FUNDAMENTAL HYDROCARBON RESEARCH

This report summarizes data relative to the properties of pure hydrocarbons compiled for the Petroleum Section of the U.S. Naval Technical Mission to Japan by Dr. S. KOMATSU of the First Naval Fuel Depot, OFUNA. These data have been obtained by Dr. KOMATSU and his associates at the Imperial Universities and Institutes throughout Japan. It is Dr. KOMATSU's contention that the chemical behavior of organic compounds can frequently be anticipated by a consideration of the physical properties. In the report which he has submitted, he discusses the application of the physical characteristics of hydrocarbons to the selection of proper treating methods in preparing hydrocarbon fuels. Fuel research programs at OFUNA utilizing these fundamental studies as theoretical background are described in reports of the U.S. Naval Technical Mission to Japan relative to the pine root oil program in Japan and to the aviation gasoline research conducted by the Japanese Navy.

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LIST OF ENCLOSURES

REFERENCES

Location of Target:

First Naval Fuel Depot, OFUNA, Kanagawa Prefecture.

Tokyo Imperial University, TOKYO.

Kyoto Imperial University, KYOTO.

Japanese Personnel Interviewed:

S. KOMATSU, Ph. D., Civilian Advisor to the Department of Fuel Research, First Naval Fuel Depot, OFUNA, (formerly Professor of Biochemistry at Kyoto Imperial University, foremost chemist of First Naval Fuel Depot).

A. IBUKI, Ph. D., Professor of Biochemistry at Kyoto Imperial University.

INTRODUCTION

For the past fifteen years Dr. S. KOMATSU has been interested in the relationship between the chemical structure and the physical properties of pure hydrocarbons. During most of this period he was Head of the Department of Biochemistry at Kyoto Imperial University, but in 1943 he came to the First Naval Fuel Depot, OFUNA, as Civilian Advisor to the Department of Fuel Research. While in OFUNA, he applied many of his theories to the research being conducted at the Depot, and related research projects which he had assigned to his co-workers at Kyoto Imperial University and Tokyo Imperial University were continued.

Enclosure A of this report was prepared at the request of the Petroleum Section of the U.S. Naval Technical Mission to Japan with the thought that it might include some new data or might serve as supporting material for that obtained by others interested in this phase of hydrocarbon research, such as the Hydrocarbon Research Committee of the American Petroleum Institute. A review of the information thus obtained shows that it includes a compilation of the data obtained by Dr. KOMATSU and his associates relative to the physical properties and cracking temperatures of some pure hydrocarbons, as well as a study of the decomposition products of these hydrocarbons by ultra-violet ray absorption spectra and Raman spectra.

While it is realized that most of this information was published in Japanese journals before the beginning of the war, and that similar studies have been duplicated in American laboratories, it was felt worthwhile to collect and present the material available at this time without attempting its appraisal.

THE REPORT

A. SCOPE OF STUDIES

The report entitled "On the Physical Properties of Some Pure Hydrocarbons," written by Dr. KOMATSU and submitted, herewith, as Enclosure (A), is made up of five parts. In Parts I and II the author discusses the use of such properties as boiling point and density or molecular volume in predicting the chemical behavior of various types of hydrocarbons. Correlations are drawn between the molecular volume and cracking temperatures of related compounds. These temperatures have been determined, and the products of decomposition have been studied by means of ultraviolet absorption spectra. Raman spectra were utilized in examining isomeric hydrocarbon mixtures and also as a means of studying the composition of gasoline distillation fractions.

Part III of Dr. KOMATSU's report is a tabulation of the properties of pure hydrocarbons as determined in Japanese research laboratories. This section includes assembled data pertaining to the boiling points, densities, refractive indices, decomposition temperatures, and decomposition products of approximately one hundred different hydrocarbons. Ninety per cent of these compounds are from the six to eighteen carbon atom range, and octane numbers of twelve of them have been determined. Of particular interest are the conjugated hydroaromatic compounds synthesized by Dr. I. KAGEHIRA of the First Naval Fuel Depot in connection with fundamental lubrication studies and discussed in detail in Enclosures (A), (B)1, and (B)2 of NavTechJap Report, "Japanese Fuels and Lubricants, Article 8 - Naval Research on Lubricants," Index No. X-38(N)-8.

Parts IV and V of the enclosed report tabulate ultraviolet absorption data for twenty-five hydrocarbons and Raman spectra data for thirty-eight hydrocarbons.

B. APPLICATION TO REFINING TECHNOLOGY

Dr. KOMATSU has indicated that the information presented in Enclosure A is of value in selecting the proper treating methods for the preparation of fuels from various types of hydrocarbons. The following comments are made relative to those portions of the paper which have application to refining techniques.

1. Boiling Point and Molecular Volume

Boiling point changes within different homologous series are discussed and correlations between these boiling points and the tendency of organic compounds to form stable groups of five or six carbon atoms are indicated. Based on this assumption, the author points out that, when normal paraffines are subjected to thermal cracking, it can be anticipated that molecules of five, six, nine, or ten carbon atoms will predominate in the distillate.

The author discusses the relationship between thermal stability and close-packing as indicated by the molecular volume. He maintains that compounds of higher density will be more stable than those of lower density with the same number of carbon atoms. In support of this assumption, the molecular volumes and decomposition temperatures are compared for two series of hydrocarbons; n-hexane, cyclo-hexane, and benzene; and ortho-, meta-, and para-xylene.

This hypothesis is also applied to catalytic rearrangements of unsaturated compounds such as the catalytic transformation of octalin to

tetralin and decalin. These reactions were discussed in detail by the author in describing the catalytic rearrangement of terpenes to naphthenes and aromatics in Enclosure (A) of NavTechJap Report, "Japanese Fuels and Lubricants, Article 4 - Pine Root Oil Program," Index No. X-38(N)-4.

2. Cracking Temperatures

The cracking or decomposition temperature of hydrocarbons has been studied by Dr. KOMATSU and his associates at Kyoto Imperial University. The method used was to heat 0.2-0.3 grams of sample in a silica reaction vessel, initially evacuated to a pressure of 0.001mm of mercury. Pressure and temperature changes were recorded as heating progressed. Cracking was indicated by sudden changes in pressure and the decomposition products were determined by gas analysis. Enclosure (B) tabulates typical data obtained with this apparatus.

These experiments have indicated, in general, that the cracking temperatures of paraffinic hydrocarbons are below 500°C, those of naphthenic hydrocarbons are usually between 500°C and 600°C, and those of aromatic hydrocarbons are above 700°C. Alkyl-aromatic hydrocarbons have two cracking temperatures--that of the side chain and that of the ring. This is also true of aromatic-naphthenic hydrocarbons, such as tetralin.

3. Ultraviolet Absorption Spectra

Dr. KATO of Tokyo Imperial University has utilized ultraviolet absorption spectra to observe the decomposition products of thermally cracked hydrocarbons. In Enclosure (A) data are presented relative to the products of thermal cracking and oxidation at different temperatures for benzene, toluene, ethyl benzene, isopropyl benzene, and tertiary butyl benzene. From data of this type the nature of the thermally cracked products of paraffines, napnthenes, and aromatics was obtained.

4. Raman Spectra

Raman spectra have been used as a means of studying the effect of heat on organic compounds. Enclosure (A) presents data obtained by using Raman spectra in examining the polymerization products of n-butene, the dehydration products of n-butanol, and the hydrocarbon constituents of gasoline. A sample of SANGA SAWA straight run gasoline was separated into 23 fractions, and the composition of each fraction was examined.