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Detroit, Michigan

MISCIBILITY AND HEALTH HAZARD OF VITOL FLUID COMPONENTS

PURPOSE

(1) To determine the temperature and dilution at which TEL (tetraethyllead) begins to separate from aqueous alcohol solutions initially containing 3 cc. TEL/gal.

(2) To determine the emulsion stability of Vitol Fluid and the TEL content of the internal and continuous phases.

SUMMARY

The separation temperatures of TEL, 62-Mix, and 1.0-T "Ethyl" Antiknock Compounds from various Vitol-like water-alcohol solutions were determined. The separation temperatures of 62-Mix fluid, at a concentration of 3 cc. TEL/gal., from aqueous solutions containing 85 vol. % methanol, ethanol, and isopropanol were -60, -73, and -30°C., respectively; as the concentration of water increased, the TEL separation temperature rose rapidly.

Aqueous solutions containing 85% alcohol and 3 cc. TEL/gal. as TEL, 62-Mix, or 1.0-T aviation fluid were diluted with water at room temperature until a phase separation occurred. Separation of TEL begins at the following alcohol concentrations: 68.2% methanol, 50.6% ethanol, and 34.9% isopropanol.

Vitol Fluid prepared according to the present formula of the Thompson Vita-Meter Corporation is a murky, yellow emulsion. Filtration of two samples through filter paper removed the internal or dispersed phase, yielding a clear, yellow filtrate of reduced TEL concentration. On standing or centrifugation, the internal phases separated as light brown lower layers containing 10 to 12% TEL. Altogether, it appears that the TEL in Vitol Fluid may be so

(Continued)

easily concentrated in the course of handling that this anti-knock fluid constitutes a much more serious health hazard than leaded gasoline of equal TEL content.

INTRODUCTION

It has long been recognized that the addition of alcohol to motor fuels reduces knock and gives generally better performance. However, for several reasons alcohol has not come into wide-spread commercial use.

The Thompson Vita-Meter Corporation has experimented with solutions of water in alcohols, and has recently developed an injection device designated the Vita-Meter. This device is designed to inject the so-called Vitol Fluid into the carburetor when the manifold pressure falls below a certain value. The present Vitol Fluid is an alcohol-water mixture containing "Ethyl" Anti-knock Compound and a rust inhibitor, such as Penola 2210, in the following proportions: 85 parts methanol, 15 parts water, 1/8 part rust inhibitor, 3/8 part kerosene, and 3 cc. TEL/gal. as 62-Mix fluid.

Since the Thompson Vita-Meter Corporation is now marketing the Vita-Meter and Vitol Fluid, it is desirable that this Laboratory evaluate this method of increasing octane number. The present work is particularly concerned with possible health hazards resulting from the use of Vitol Fluid; current experiments on the storage stability and the air evaporation of the fluid will be reported in subsequent LTD's.

EXPERIMENTAL

Separation of TEL from Alcohol-Water Solutions

As an introduction to the study of Vitol Fluid, a study was first made of the solubility and separation temperatures of TEL from various alcohol-water mixtures.

The clouding or initial freezing points of various mixtures of water and alcohols containing 3 cc. TEL/gal. as straight TEL, 62-Mix, or 1.0-T aviation fluid, are presented in Table I. As the concentration of water increases, the TEL separation temperature rises rapidly.

TABLE I - Separation of Leaded Alcohol-Water Solutions

Alcohol		Separation temperature, °C., for solution containing 3 cc. TEL/gal. as		
Kind	Vol. %	TEL	62-Mix	1.0-T Mix
Methanol	85	-40	-60	-63
Ethanol	85	-74	-73	-54(a)
Isopropanol	85	--	-30(a)	-26(a)
Methanol	75	-2	--	25
Ethanol	75	-71(a)	-36(a)	-36(a)
Isopropanol	75	-37(a)	--	-21(a)
Methanol	50	--	25	25
Ethanol	50	--	25	25
Isopropanol	50	--	-21(a)	-16(a)

(a) Separated phase was solid.

Dilution of Vitol-Type Fluids

The extent to which 85% alcohol solutions containing 3 cc. TEL/gal. as TEL, 62-Mix, or 1.0-T aviation fluid can be diluted with water before a second phase separates was also determined. These data, obtained by titrating 25-ml. samples with water, and comparable data, supplied by the Thompson Vita-Meter Corporation, are given in Table II.

TABLE II - Separation of Vitol-Type Fluid on Dilution with Water

Alcohol (85 vol. %)	TEL Added As	Concentration, % alcohol	
		Ethyl Data	Thompson Data
Methanol	TEL	69.3	--
"	62-Mix	68.2	73.5
"	1.0-T Mix	69.8	--
Ethanol	TEL	51.2	--
"	62-Mix	50.6	55.1
"	1.0-T Mix	52.2	--
Isopropanol	TEL	36.3	--
"	62-Mix	34.9	38.5
"	1.0-T Mix	35.3	--

These data show that, of the three alcohols tested, isopropanol is the most effective with respect to solubilizing TEL in water and that methanol is the least effective.

In the tests in which 62-Mix fluid was used, separation occurred at 68.2, 50.6, and 34.9% alcohol, in methanol, ethanol, and isopropanol solutions, respectively. These values are from 3.6 to 5.3% lower than the corresponding values reported by Thompson Vita-Meter Corporation, which represents a greater discrepancy than would be expected. Perhaps the Thompson data show the minimum alcohol content of alcohol-water systems at which 3 cc. TEL/gal. of the antiknock compound is soluble, whereas the data obtained at this Laboratory represent the minimum alcohol content at which the antiknock compound added at 3 cc. TEL/gal. to an 85% alcohol solution remains in solution when the entire system is diluted with water.

Study of Present Vitol Formula

A 1-gal. sample of Vitol Fluid was prepared according to the directions furnished by the Thompson Vita-Meter Corporation, except that No. 9 oil (refined kerosene) was used instead of ordinary kerosene. The resulting Vitol Fluid was a murky, yellow liquid having a density, d_4^{20}, of 0.8428. Analysis indicated that it contained 3.23 g. Pb/gal., or 3.06 cc. TEL/gal. On standing, a small amount of a lower layer separated from the sample. This was surprising since the Thompson Vita-Meter Corporation reported that Vitol Fluid is an emulsion that is completely stable either on standing or on centrifugation. Subsequently, a sample of commercial Vitol Fluid received from the Thompson Vita-Meter Corporation also separated into two distinct phases on standing or centrifugation. In contrast, a sample prepared at this Laboratory containing only 1 cc. TEL/gal. did not separate when subjected to either treatment.

Two methods were used to study the TEL distribution between the two liquid phases of the Vitol solution. The first method was to filter a 200-ml. sample through three thicknesses of filter paper. This treatment removed the internal phase yielding a clear yellow solution as the filtrate. Analysis then showed that approximately 12% of the TEL was removed in the internal phase.

Anal: Vitol solution, 3.23 g. Pb/gal.; filtrate, 2.84 g. Pb/gal.

In the second method a 300-ml. sample of Vitol Fluid was centrifuged at 1800 r.p.m. for 30 min. The bulk of the material remained as a murky yellow liquid. However, approximately 0.15 g. of a light brown liquid separated as a lower layer. On analysis this lower layer was found to contain 7.5% lead, or 11.7% TEL.

Similarly, the TEL distribution in a sample of commercial Vitol Fluid received from the Thompson Vita-Meter Corporation was investigated as follows. A 2-gal. sample of the material (containing 2.87 g. Pb/gal.) was allowed to stand for three days, during which time part of the internal phase coalesced into larger droplets which were concentrated at the bottom of the container. The upper layer, a murky yellow liquid was removed. A 500-ml. portion was clarified by filtration through three thicknesses of filter paper; the filtrate contained 2.43 g. Pb/gal. (2.30 cc. TEL/gal.). The lower layer, consisting of a high concentration of the suspended phase as droplets, was transferred to a 100-ml. tube and centrifuged for 2 hr. at 1800 r.p.m. A 10.0-ml. quantity of clear yellow oil separated, of which 9.0 ml. (7.3 g.) was isolated. This material analyzed 6.46 wt. % lead. The information relative to the TEL distribution is summarized in Table III.

TABLE III - TEL Distribution in Vitol Fluid

Vitol Fluid	Laboratory Blend	Commercial Sample
g. Pb/gal.	3.23	2.87
cc. TEL/gal.	3.06	2.72
Continuous Phase		
g. Pb/gal.	2.84	2.43
cc. TEL/gal.	2.68	2.30
Internal Phase		
Wt. % Pb	7.47	6.46
Wt. % TEL	11.7	10.1
g. Pb in phase/gal. (a)	0.39	0.44
Wt. of phase, g./gal. (b)	5.22	6.81
Vol. of phase, cc./gal. (c)	6.2	8.1
% of total TEL in phase (b)	12.1	15.3

(a) Determined by difference.
(b) Calculated values.
(c) Assuming a density of 0.84.

The TEL distribution data for the two samples are in reasonably close agreement, showing that from 12 to 15% of the TEL is in the internal phase, and that the TEL content of this phase is high enough, approximately 11%, to be quite hazardous.

Reference: Notebooks 1592 and 1 16

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