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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

MEMORANDUM REPORT

for the

Army Air Forces, Materiel Command

LOSS OF XYLIDINES IN OVERWATER STORAGE OF XYLIDINE-BLENDED FUEL

By Walter T. Olson and Adelbert O. Tischler

SUMMARY

The purpose of the tests made were twofold: (a) To determine the relationships for estimating the maximum amount of a water-soluble gasoline additive that will diffuse from the gasoline to the water when the fuel is stored over water and (b) to determine from these relationships the amount of xylidines that will diffuse from the gasoline to the water in an overwater-storage system. A physical expression for the loss of water-soluble additive was derived for each of the following conditions of storage-tank operation:

(1) Equilibrium distribution of additive between the two layers is nearly attained during the period between successive additions or withdrawals of the fuel but, during the actual addition or withdrawal of fuel, no significant transfer of additive occurs between the gasoline and water layers.

(2) Equilibrium distribution of additive between the gasoline and the water layers exists at all times.

The estimated values of xylidines concentration in fuel stored over water were checked against such experimental data that exist.

The derived formulas for estimating the loss of water-soluble additive in overwater gasoline storage check reasonably well with the experimental data available.

The estimated loss of xylidines from gasoline stored over water for the conditions of storage-system operation indicated are as follows:

PERCENTAGE DECREASE OF ORIGINAL CONCENTRATION OF XYLIDINES IN GASOLINE
[Distribution coefficient, $K = 20$]

Volume percentage of original fuel remaining in tank	Condition		
	Continuous equilibrium	Each batch removed, 10 percent of tank volume	Single batch removed
80	1	1	1
50	3	4	4
20	7	8	17
10	10	12	31
1	14	19	85

The data indicate that the losses of xylidines from gasoline stored over water would not be excessive provided that not more than 80 percent of the fuel was replaced by xylidine-free water.

INTRODUCTION

When gasoline containing a water-soluble additive, such as xylidines or another aromatic amine, is stored in contact with water as is the case in the widely used overwater-storage systems, the water extracts a certain amount of the additive from the gasoline. This report presents relationships for estimating the concentration of additive as a function of the volume of gasoline stored in an overwater system and evaluates from these relationships the suitability of xylidine-blended fuel for overwater storage.

Although it is unlikely that a single satisfactory equation for use under all conditions encountered in practice can be written, certain assumptions permit mathematical derivations of expressions for the concentration of additive in fuel stored over water. An expression for the concentration of xylidines in gasoline stored over water had previously been given in a memorandum by the Petroleum Administration for War. One object of the present analysis is to determine a suitable expression that covers a wider range of situations than does the equation presented in this memorandum.

A secondary object of the analysis is to present an equation that can be applied to the operation of the overwater-storage system where numerous very small batches of fuel are successively removed from the tank, for example, in servicing aircraft directly from a

large overwater-storage tank. The results of a test on a full-scale, overwater-storage system conducted with xylidine-blended fuel by the Army Air Forces (Rep. No. ENG-57-531-216) provide an incomplete check on the derived relationships for additive concentration.

The analysis was performed at the Aircraft Engine Research Laboratory of the National Advisory Committee for Aeronautics during June 1943 and January 1944.

ANALYSIS

In the operation of an overwater-storage-system tank, fuel is withdrawn from the tank by adding water at the bottom of the tank and fuel is added to the tank by the removal of storage water from the tank. The tank contains two phases, one of gasoline and one of water, and is full of liquid at all times.

Assumptions

In the determination of the expressions for the concentration of additive in fuel stored over water at any volume of fuel, the following assumptions apply to the analyses:

1. When equilibrium conditions are reached, the distribution law applies to the additive; namely, the ratio between the concentrations of the additive in the two phases of the gasoline-water system is constant at constant temperature. The ratio is described as the distribution coefficient and defined as

$$K = \frac{\text{additive concentration in gasoline phase}}{\text{additive concentration in water phase}}$$

This constant must be experimentally determined for each additive. It varies with temperature of the fuel and water and with the nature of the fuel. Any variation in the distribution coefficient caused by additive concentration may be assumed to be negligible in the range of concentrations produced by the distribution process.

2. The volume of the additive itself, when present to the extent of 2 or 3 percent or less, is negligible by comparison with the volumes of gasoline and water. The equilibrium concentration is the minimum concentration of additive in the fuel at the volume in question.

Symbols

The following symbols are used in the analyses:

K	gasoline-water distribution coefficient (experimentally determined)
X	concentration of additive in gasoline before addition or removal of portion of fuel
X'	concentration of additive in gasoline after addition or removal of portion of fuel (at equilibrium)
V	volume of storage tank
V_g	volume of fuel in tank before addition or removal of portion of fuel
V_g'	volume of fuel in tank after addition or removal of portion of fuel
V_w	volume of water in tank before addition or removal of portion of fuel
V_w'	volume of water in tank after addition or removal of portion of fuel
V_f	volume of fuel added or withdrawn ($V_f = V_g' - V_g$)
Z	concentration of additive in fuel added or withdrawn
Y	concentration of additive in water added or withdrawn

Derivations

Because the manner in which an overwater-storage system is operated is one of the most important variables influencing the additive concentration in the stored fuel, two cases representing two very different operating procedures have been studied.

Case 1. -- Case 1 is intended to apply to successive additions or withdrawals of fuel stored in contact with water when an appreciable period of time has elapsed between each addition or withdrawal.

This situation will be approximated by assuming that, during the actual addition or withdrawal of fuel, no additive is transferred between the gasoline and water phases but that equilibrium distribution of additive between the two phases is attained during the period between successive additions or withdrawals of fuel. This assumption is made on the basis that the rate of diffusion of additive between the two phases is slow. Obviously, the longer the period between additions or withdrawals of fuel, the more precisely will the equation agree with the actual situation. (Quantity of additive in gasoline after addition or withdrawal of fuel but before equilibrium) + (quantity of additive in water after addition or withdrawal of fuel but before equilibrium) = (quantity of additive in gasoline after equilibrium) + (quantity of additive in water after equilibrium).

$$\left(XV_g + ZV_f \right) + \left(\frac{XV_w}{K} - YV_f \right) = X' (V_g + V_f) + \frac{X'}{K} (V_w - V_f) \quad (1)$$

If the terms are expanded and collected

$$X' = \frac{KXV_g + KZV_f + XV_w - KYV_f}{KV_g + KV_f + V_w - V_f} \quad (2)$$

which is for general use.

If fuel is displaced from the tank by fresh water, $Z = X$, $Y = 0$, $V_g' = V_g + V_f$, and $V_w' = V_w - V_f$. Then

$$X' = X \left(\frac{V_w + KV_g'}{V_w' + KV_g'} \right) \quad (3)$$

Case 2. - Case 2 applies to successive small withdrawals of overwater stored fuel over an appreciable length of time. In order to approximate this situation, it is assumed that equilibrium distribution of additive between gasoline and water exists at all times. An equation of this sort permits evaluation of additive concentration under circumstances where withdrawals of fuel have been small, compared with the tank capacity, but very numerous. The equation may thus be considered as the result of applying the equations of case 1 to an infinite number of steps, with equilibrium established between each step. (Quantity of additive in fuel stored over water) + (quantity of additive in water) = (quantity of additive in stored

fuel before removal of small increment) + (quantity of additive in water before addition of increment of fresh water) + (quantity of additive removed in small increment of fuel). Let $\Delta X = X' - X$, $\Delta V_g = V_g' - V_g$, and $\Delta V_w = V_w' - V_w$.

$$X' V_g' + \frac{X' V_w'}{K} = X' - \Delta X (V_g' - \Delta V_g) + \left(\frac{X' - \Delta X}{K} \right) (V_w' - \Delta V_w) + (X' - \Delta X) \Delta V_g \quad (4)$$

If second-order differentials are removed, equation (4) can be expanded and simplified:

$$-X' \Delta V_w = \left(K V_g' + V_w' \right) \Delta X \quad (5)$$

But $\Delta V_w = \Delta V_g$ and $V_w' = V - V_g'$. Therefore,

$$\frac{\Delta X}{X'} = \frac{\Delta V_g}{V_g' (K - 1) + V} \quad (6)$$

By integration from any concentration X and volume V_g to X' and V_g'

$$X' = X \left(\frac{V_g' (K - 1) + V}{V_g (K - 1) + V} \right)^{\frac{1}{K-1}} \quad (7)$$

DISCUSSION

Recently a full-scale, overwater-storage test of xylidine-blended fuel was conducted by the Army Air Forces. In this test, 8105 gallons of aviation fuel were stored in a water-displacement tank of 25,000-gallon capacity and immediately samples and analyzed. Periodically, the stored gasoline was sampled and analyzed and part of the stored fuel was removed. Because the process is a "batch" process, equation (2) is applicable. The test provides an evaluation of the equation for the particular conditions.

For an assumed average temperature of the tank contents of about 65° F and for fuel displacement with fresh water, a volume distribution coefficient of 17 was selected for xylidines from reference 1.

Table 1 compares the results of the full-scale, water-system test with the equilibrium concentration as calculated from equation (2). For this particular test, the calculated results agreed well with the experimental data.

TABLE 1. - STORAGE-SYSTEM TESTS

Sample taken ^a	May 27	June 7	June 19	July 3	July 13 1943
Fuel in tank before removal of batch, gal	8105	8105	6105	2105	1105
Water in tank before removal of batch, gal	16,895	16,895	18,895	22,895	23,895
Fuel removed, gal	(fuel placed in storage system)	2000	4000	1000	1105
Xylidines, grams/100 ml (electrometrically)	1.05 Mean $\frac{1.05 + .98}{2} = 1.01$	(b)	0.94 .826 .826 .82	0.825 .83	0.815 .82 (c)
Equilibrium concentration, X'	(calculated from equation (2))	^d 0.900	^e 0.886	0.825	0.806

^aAnalysis indicated under each date is prior to removal from the storage tank of the quantity of fuel indicated under that date.

^bSample was inadvertently mixed with some xylidine-free fuel.

^cThe fuel stored over water gave a negligible decrease in knock ratings.

^dSample calculation for run on June 7. - Because the tank contained no fuel prior to the addition of the 8105 gallons on May 27, $V_g = 0$, $X = Q$, and $Y = 0$. Therefore, from equation (2)

$$X' = \frac{(17)(1.01)(8105)}{(17)(8105) + 25,000 - 8105} = 0.900 \text{ (equilibrium concentration attained on standing)}$$

^eSample calculation for run on June 19. - In this case, $Z = X$ and $Y = 0$. Equation (2) therefore becomes equation (3) and

$$X' = 0.900 \left(\frac{16,895 + (17)(6105)}{18,895 + (17)(6105)} \right) = 0.886$$

Figure 1 shows normally anticipated additive concentration in fuel stored over water for three different types of operation of overwater-storage tanks. A volume distribution coefficient of 20 is assumed, inasmuch as experimental values ranged from 13 to 26 for xylidines (reference 1). One of the curves represents fuel displaced from a full tank in successive small increments over a period of time sufficiently long for equilibrium to exist at all times; it is a plot of equation (7). The curve that indicates the concentrations expected if fuel is displaced from a full tank in successive quantities (each 10 percent of the total tank volume) and if equilibrium exists between fuel withdrawals is derived from equation (2). The curve for a single batch removed shows the concentration expected if fuel is displaced from a full tank in a single, fairly rapid operation with equilibrium established only after the withdrawal operation; it also shows the resulting concentration when a batch of fuel is added to a tank containing additive-free water.

Under most circumstances, loss of an additive with a distribution coefficient of about 20, such as xylidines, by extraction with storage water will not be severe. Excessive loss of xylidines from the fuel to storage water will occur when the tank contains a ratio of xylidine-free water to fuel in excess of about 4:1. Consequently, use of a small batch of fuel remaining after the previous withdrawal of 80 percent or more of the stored fuel and storage over additive-free water of a volume of fuel 20 percent or less of the tank volume are to be avoided.

The equations presented will apply only to the extent that the assumptions made in deriving the equations pertain to the particular application. In practice, varying temperature, varying gasoline-water interface area, and varying frequency and quantity of additions and withdrawals of fuel make it practically impossible to know the exact distribution relationship of xylidines, or any additive, between the gasoline and water phases at all times. The equations, nevertheless, do provide useful approximations.

SUMMARY OF RESULTS

The derived formulas for estimating the loss of water-soluble additive in overwater gasoline storage check reasonably well with the experimental data available.

The estimated loss of xylidines from gasoline stored over water for the conditions of storage-system operation indicated are as follows:

PERCENTAGE DECREASE OF ORIGINAL XYLIDINES CONCENTRATION IN GASOLINE
[Distribution coefficient, $K = 20$]

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80	1	1	1
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10	10	12	31
1	14	19	85

CONCLUSION

The data indicate that the losses of xylidines from gasoline stored over water would not be excessive provided that not more than 80 percent of the fuel was replaced by xylidine-free water.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, March 18, 1944.

REFERENCE

1. Tischler, Adelbert O., Slabey, Vernon A., and Olson, Walter T.: Gasoline-Water Distribution Coefficients of Xylidines. NACA Memo. rep., June 29, 1943.

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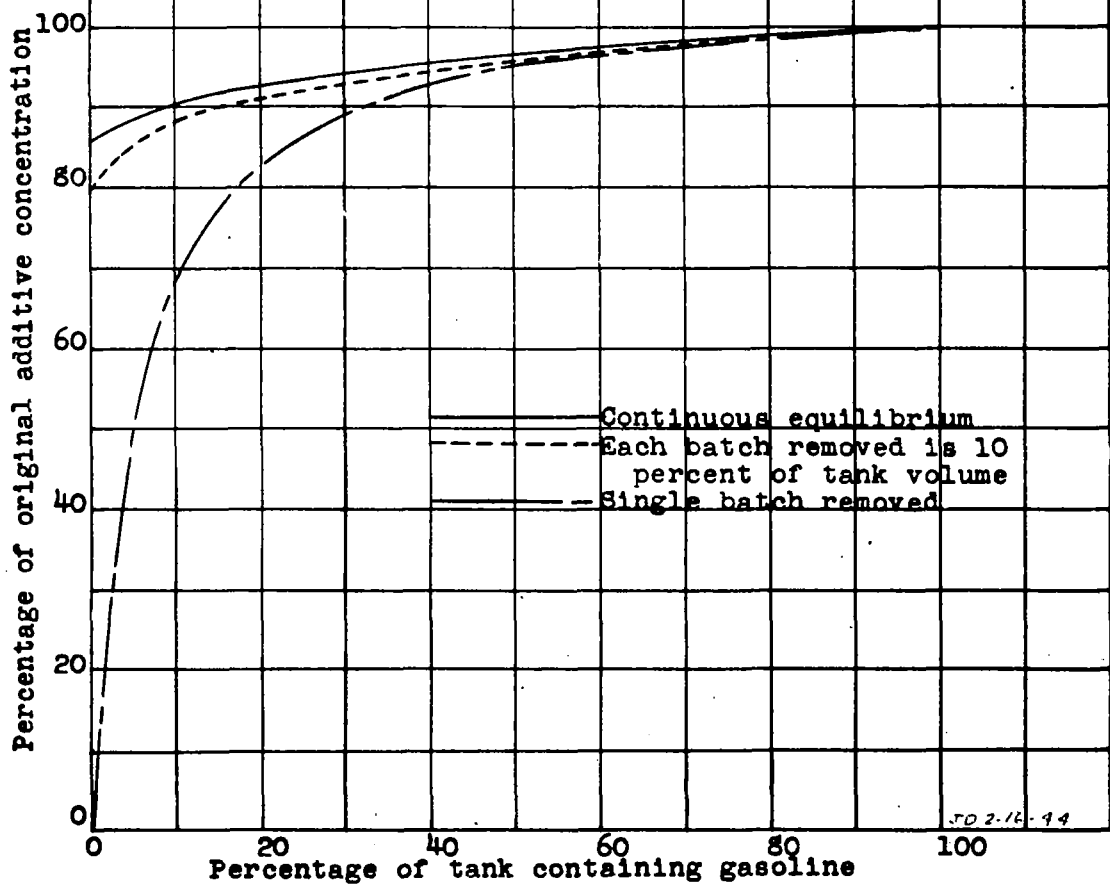


Figure 1. - Additive concentration in gasoline stored over water.
 $k = 20$.

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ABSTRACT:

Tests were made to determine relationships for estimating maximum amounts of water soluble gasoline additive that will diffuse from gasoline to water when fuel is stored over water and to determine from these relationships the amount of xylidines that will diffuse from the gasoline in the same type of storage. Data indicate that losses of xylidines from gasoline stored over water would not be excessive provided that not more than 80% fuel was replaced by xylidine-free water.

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