See p 10
11

Miscellaneous Hazard No. 2498
Application No. 32C1907

February 3, 1934.

REPORT

on

LUBRICANT

Swann Chemical Co.,
New York, N.Y.

Swanco 80 ... 100 ... 16 ...

MONS 060198

TABLE OF CONTENTS

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Miscellaneous Hazard No. 2498
Application No. 32C1907

February 3, 1934

REPORT

on

LUBRICANT

Swann Chemical Co.,
New York, N.Y.

DESCRIPTION

GENERAL CHARACTER AND USE:

The product, which is the subject of this report, is a synthetic oil consisting of a mixture of chlorinated hydrocarbons. It is made in several grades having different viscosities. The color of the three grades submitted varies from light yellow to deep golden yellow. It is intended for use as a general lubricant and particularly for the lubrication of steam turbines operating with high temperature steam.

MARKING:

"Swanco", 80 to 150, stenciled on containers.

CLAIMS MADE FOR THE PRODUCT

The manufacturer claims that the product is a distinct improvement in lubricating oils in respect to fire hazard. It has no fire point and is relatively nonflammable.

PLAN OF INVESTIGATION

The object of this investigation was to determine the nature of the recommendation to be made relative to the fire and toxic hazard of the product.

In planning the investigation consideration was given to the General Nature of the product, its Fire and Toxic Hazard, Stability, and Uniformity. The manner of investigation of each of these phases is given below.

GENERAL NATURE:

Information as to the general nature of the product was obtained by means of Identification Tests.

FIRE AND TOXIC HAZARD:

The fire hazard of the product was investigated in respect to flammability, ignition temperature, explosibility, and decomposition temperature. The products of decomposition were investigated in respect to flammability and explosibility. Consideration was also given to the toxicity of the fumes produced on contact with flame or by decomposition of the product. These features were covered by Flash Point Tests, Fire Point Tests, Vapor Pressure Determinations, Ignition Temperature Tests, Explosibility of Vapors Test in specially designed apparatus, Explosive Range Tests, and Analytical Tests of Products of Decomposition.

STABILITY:

Information on this phase of the investigation was obtained from the Decomposition Tests and from consideration of the chemical nature of the product.

UNIFORMITY:

As the methods of manufacture are subject to reasonably definite control, a detailed investigation of this feature was not required.

E X A M I N A T I O N A N D T E S T R E C O R D

DESCRIPTION OF SAMPLES

The manufacturer supplied for testing the following samples:

1 can (12 lb.) "Swanco 80"
2 cans (24 lb.) "Swanco 100"
1 can (12 lb.) "Swanco 150"

The first and last samples were furnished as representative respectively of the minimum and maximum chlorine content, corresponding to the minimum and maximum viscosity of the product suitable for lubrication of modern steam turbines. The second sample was supplied as one between the other two in chlorine content and viscosity.

For use in comparative tests two samples of ordinary commercial turbine oil were obtained by Underwriters' Laboratories. These samples are designated as Sample "A" and Sample "B".

IDENTIFICATION TESTS:

METHODS

Specific Gravity - The specific gravity at 15.6 C(60 F) with respect to water at the same temperature was determined by means of a pycnometer.

Flash Point - The flash point test was made with the Pensky-Martens closed cup tester, using the standard A.S.T.M. method for this instrument.

Fire Point - The fire point test was made with the Cleveland open cup tester, using the standard A.S.T.M. method for this instrument.

Viscosity - The viscosity at 122 F was determined by means of the Saybolt Universal Viscosimeter according to the standard A.S.T.M. method for this instrument.

Acidity - The acidity of the oil was determined by heating a 20-g. sample with alcohol and titrating with standard fiftieth normal base, using phenolphthalein as an indicator. The acidity was calculated in terms of per cent HCl by weight.

Qualitative Test for Chlorine - A small sample (No. 100) was tested with metallic sodium by heating in a test tube. The test tube was broken in water, and the solution filtered. The filtrate was acidified with nitric acid and silver nitrate solution added. The presence of chlorine is shown by a white precipitate.

Distillation - The distillation was conducted employing the A.S.T.M. Method for Distillation of Gas Oils (D 158) except that temperature and volume readings were more frequently taken.

Determination of Chlorine - The percentage chlorine was determined by the Carius method.

RESULTS

The results are tabulated below:

Determination	"Swanco 80"	"Swanco 100"	"Swanco 150"	A	B
Specific Gravity at 60 F / 60 F	1.461	1.479	1.485	0.884	0.889
Flash point, deg.F Pensky-Martens	395*	405*	395*	370	390
Fire point, deg.F Cleveland open cup	None**	None**	None**	450	460
Viscosity Saybolt Universal at 122 F	(no test)	121	(no test)	(no test)	(no test)
Acidity, per cent HCl by weight	(no test)	0.0012	(no test)	(no test)	(no test)
Qualitative test for chlorine	(no test)	present	(no test)	(no test)	(no test)

* In view of the negative results obtained in the Fire Tests, it is clear that the flash point test cannot be depended upon to give a true measure of the fire hazard of this product. It was therefore necessary to conduct tests of the explosibility of the vapors of the product in specially designed apparatus - see page 9 et seq. (See "Underwriters' Laboratories' Method for the Classification of the Hazards of Liquids", page 4 et seq.)

** Intermittent flashes were obtained but the product did not continue to burn. The sample was heated to boiling point; the test was then discontinued.

Determination

Distillation, Sample No. 100.

Temperature F	Temperature C	Volume Cubic Centimeters	Per Cent by Volume
647.0	341.4	1st drop	0.0
650.0	343.3	46	23.0
655.0	346.1	57	28.5
660.0	348.9	33	16.5
665.0	351.7	21	10.5
670.0	354.5	16	8.0
675.0	357.2	8	4.0
680.0	360.0	6	3.0
685.0	363.0	4	2.0
690.0	366.0	4	2.0

Volume distilled	200 cc.
Initial boiling point	647 F(341.4 C)
Maximum temperature	690 F(366.0 C)
Recovered	97.5 per cent
Residue and loss	2.5 per cent

Determination of chlorine - The per cent chlorine was found to be in accord with manufacturer's statement.

VAPOR PRESSURE DETERMINATIONS:

SAMPLE

"Swanco 100" was used in these tests.

METHOD

The Hoffmann apparatus and method were employed in these determinations. The apparatus consists essentially of a graduated barometer tube filled with mercury and surrounded by a glass jacket. The glass jacket is provided with an inlet for heated vapors and an outlet for the heated vapors and condensate. A thermometer is suspended in the vapor space between the barometer tube and glass jacket.

In conducting the test, the height of the mercury in the barometer tube was measured, and the sample was then introduced into the tube, and allowed to remain at room temperature over night. In the morning the height of the mercury in the tube was again measured. The temperature of barometer tube and sample was next raised, furfural vapor, introduced at the top of the jacket, being used as a heating medium. After the temperature became constant, the height of the mercury in the tube was measured and the barometric pressure noted. From these data the vapor pressure at the boiling point of furfural was calculated applying correction for temperature and the vapor pressure of the mercury. The test was repeated, using naphthalene vapor and benzoic acid vapor as heating mediums.

RESULTS

The results of the tests are tabulated below:

Boiling Substance	Temperature C	Vapor Pressure Mm. of Hg.
furfural	159.0	4
naphthalene	217.5	23
benzoic acid	250.0	53

IGNITION TEMPERATURE TESTS:

METHOD

In the first series of tests, the apparatus employed consisted essentially of a conical quartz or glass flask, which was submerged to a depth equal to two-thirds of its height in a molten solder bath heated by three blast burners, and equipped with a thermocouple for temperature measurements. The flask was 1-1/8 in. in diameter at the top, 2-3/8 in. in diameter at the base, and 4-1/4 in. high, with a capacity of about 160 cc.

Tests were also conducted using an iron flask of the same size and shape.

The test consisted in dropping a few drops of the lubricant into the flask at each interval of 5 C(9 F) and observing whether or not ignition was obtained. In some of the trials a little additional air was introduced into the flask by means of a rubber bulb and bent delivery tube. After each trial the gases and vapors were completely displaced by the aid of a slow stream of air. The lowest temperature at which ignition (without application of flame) could be obtained was taken as the ignition temperature.

In the second series of tests the apparatus used consisted essentially of an iron plate 10 in. square by 1/4 in. thick, heated by means of gas burners. A sheet iron shield was provided around the plate to deflect the hot burner gases. The shield consisted of a strip of sheet iron about 10 in. wide which was bolted around the edge of the plate at an asbestos gasketed joint. The plate assembly was set upon a fire brick structure designed to conserve the heat of the burners. A calibrated 14 B.&S. gauge chromel-alumel thermocouple, brazed at the center of the upper surface of the plate and connected with a potentiometer, was used to measure the temperature of the plate.

In conducting tests the plate was heated and measured quantities of lubricant (up to 10 cc.) were applied to the center of the plate. In some tests a slow stream of compressed air was applied to the vaporizing oil. The lowest temperature at which ignition occurred was recorded as the ignition temperature.

As a check on thermocouple temperature readings, readings of plate temperature were made by means of a disappearing filament optical pyrometer.

RESULTS

The results are given in the table below:

Sample	Ignition Temperature*			Heated Plate	
	Apparatus with Flask of				
	Glass	Quartz	Iron	C	F
No. 80	no test	672 C(1243 F)	no test	770	1418
No.100	" "	661 C(1222 F)	642 C(1188 F)	770	1418
No.150	" "	no test	no test	770	1418
A	256 C(493F)	" "	" "	417	783
B	261 C(502F)	" "	" "	417	783

*Within experimental error the optical pyrometer and the thermocouple gave the same readings for plate temperature.

EXPLOSIBILITY OF VAPORS TEST:

SAMPLE

"Swanco 100" was used in this test.

METHOD

The apparatus used for this test was a specially designed steel cylinder, about 26 in. in length and 6 in. in diameter, provided with an inlet for the introduction of air and an outlet discharging to the atmosphere. A small mica observation window was provided in the wall of the cylinder. A 1/4-in. spark gap was placed at its geometric center. The cylinder was heated externally by gas burners. An iron-constantan thermocouple connected with a potentiometer was used for measuring the relative temperature of the interior of the cylinder.

In conducting a test the cylinder was heated to the predetermined temperature, and a quantity of oil (from 3 to 20 cc.) was introduced into it through a threaded hole 7 in. from one end. The hole was loosely closed, and sparks were passed across the

spark gap at half-minute intervals for a period of 15 min., or until ignition occurred. In case of negative results for 15 min., a little additional air was then added to the vapors, and sparks were again passed. The cylinder was then thoroughly purged with air in preparation for the next test.

RESULTS

The lowest temperature at which a flame propagation occurred was 166 C(331 F). This was obtained with 19 cc. of the product upon introduction of a little additional air immediately after the end of the 15-min. period. The flame propagated slowly through the mixture in the pipe, and there were no obvious pressure effects. No propagation of flame was obtained in six tests conducted at temperatures ranging from 153 to 159 C(307 to 318 F), employing various quantities ranging from 3 to 20 cc. of the product.

The explosions gradually increased in force with increasing temperature until at 250 C(482 F) moderate pressure effects were obtained as indicated by blowing asbestos plugs from openings in pipe.

EXPLOSIVE RANGE TESTS:

SAMPLES

"Swanco 80" and "Swanco 100" were used in these tests.

METHOD

The apparatus consisted essentially of a glass chamber equipped with a spark gap and a stirrer. The chamber is cylindrical with the lower end hemispherical, and is approximately 3 in. in diameter by 8 in. in height; it has a volume of 1000 cc. The apparatus is provided with a glass lid supporting the stirrer and the leads to the spark gap near the bottom of the chamber. An opening in the lid is provided for introduction of the sample. The glass chamber is immersed in a molten solder bath to a depth of 6 in.

In conducting tests the solder bath was adjusted to a temperature of 400 C(752 F), a measured quantity of the liquid to be tested was placed in the apparatus, and the vapors stirred. Sparks were then passed at the spark gap while observations were made for flame travel and pressure effects. Following the test the vapors were displaced by a slow stream of compressed air in preparation for the next test.

RESULTS

The explosive range of the product ("Swanco 100") in air at 400 C was found to be from 0.045 cc. (1.2 per cent by volume) to 0.115 cc. (3.2 per cent by volume). The percentages by volume are calculated on the basis of a molecular weight of 299.3.

Check tests with "Swanco 80" indicated a range slightly wider than that obtained with "Swanco 100".

ANALYTICAL TESTS OF PRODUCTS OF DECOMPOSITION:

This series of tests was conducted to determine the chief constituents of the products of decomposition obtained in the presence of hot-iron surfaces and also in the presence of gas flames.

SAMPLE

"Swanco 100" was used in these tests.

METHODS

The specially designed steel cylinder previously described under "Explosibility of Vapors Test" was also used in these tests. Connections for withdrawing samples of the decomposition products for analysis were inserted in the outlet pipe. An evaporating dish for the sample, a small gas burner, and a spark gap to ignite the gas at the burner were placed inside the cylinder at the small mica observation window.

Free chlorine, hydrochloric acid, phosgene, carbon dioxide, carbon monoxide, and oxygen were determined, employing the following methods.

Free chlorine was determined by aspirating a measured sample through potassium iodide solution and titrating the liberated iodine with fiftieth normal sodium thiosulphate.

Hydrochloric acid was determined by aspirating a measured sample of the gas through water in contact with a small amount of mercury, and precipitating the hydrochloric acid in the aqueous solution as silver chloride. The per cent by volume hydrochloric acid in the sample was calculated from the weight of silver chloride and the volume of the original sample.

Phosgene was determined by aspirating a measured quantity of sample through a U-tube filled with crushed antimony (to remove free chlorine) and then through a saturated solution of aniline in water. The precipitated diphenylurea (if any) was dried and weighed and the per cent phosgene calculated, one molecule of diphenylurea being equivalent to one molecule of phosgene.

Carbon dioxide, carbon monoxide, oxygen, and methane were determined by means of an Orsat apparatus with a separate hot wire combustion pipette.

Test 1 - In this test the cylinder was heated to a temperature of about 459 C(858 F) and a sample of 50 cc. of the product was introduced into the cylinder. The aspirators were then started, and samples for chlorine, hydrochloric acid, and phosgene were drawn during evolution of any considerable quantity of vapor from the outlet pipe. Two gas samples for the determination of carbon dioxide, carbon monoxide, oxygen, and methane, were taken, one at 4, and one at 24 min. after insertion of the sample of the product into the cylinder. At the end of 33 min. after introduction of the sample the fumes decreased, and aspirators were stopped.

Test 2 - A 75-cc. sample of the product was placed in the cylinder, and the small gas burner was lighted by means of a spark and was kept burning during the test by lighting again whenever extinguished. The pipe was heated to a temperature of 340 C(644 F) and,when flames began to flash from the small burner over the surface of the lubricant, the aspirators were started and samples drawn for a period of 23 min., at which time vapors ceased to come from the outlet pipe in material quantities. Samples were also taken at 6 and at 19 min. for general gas analyses.

RESULTS

The results of the tests are given in Table I. It will be observed that the gases produced by decomposition of the product included 0.6 per cent carbon monoxide, 0.99 per cent hydrochloric acid gas, and 2.1 per cent combustible gas calculated as methane.

DECOMPOSITION TEMPERATURE TESTS:

SAMPLE

"Syanco 100" was used in these tests.

METHOD

The apparatus and method described in Ignition Temperature Tests using a flask were employed in these tests, except that observations were made for decomposition rather than for ignition. Moist litmus paper was held in the vapors evolved from oil dropped into the quartz flask, and the lowest temperature at which appreciable reddening of the paper took place in a short time (about 3 min.) was taken as the decomposition temperature.

RESULTS

Decomposition of the product was not appreciable at temperatures below 400 C(752 F), but became increasingly apparent at higher temperatures.

TABLE I
GASEOUS PRODUCTS OF DECOMPOSITION OF THE LUBRICANT

	Analysis of Products of Decomposition			
	Test 1		Test 2	
Time sample was taken, min. after start of test (a)	4	24	6	19
Per cent CO_2	1.7	0.4	5.4	2.4
" " O_2	18.3	19.5	13.2	17.4
" " CO	0.4	0.3	0.6	0.5
" " CH_4 (b)	2.1	0.0	0.7	0.0

The figures given below are based on samples drawn continuously during the test.

	Test 1	Test 2
Per cent HCl	0.28	0.99
" " $COCl_3$	none	none
" " Cl_2	0.003	0.001

(a) The start of the test is taken as the time when fumes become plentiful, and when aspirators were started.

(b) While calculated as methane this figure includes other gaseous hydrocarbons also.

DECOMPOSITION TEST AT ELEVATED TEMPERATURE AND PRESSURE:

SAMPLE

"Swanco 100" was used in these tests.

METHOD

The apparatus used in these tests was a closed system of piping, having a total volume of 750 cc. It consisted of a 36-in. section of 1-in. pipe connected at right angles to a 6-in. section of 2-in. pipe. The system was provided with a gauge for measurement of the internal pressure and with an inlet for introduction of compressed air. The section of pipe 1 in. in diameter was mounted in an electrically heated test furnace 12 in. in length. A thermocouple connected with a potentiometer was used to measure the temperature of the pipe.

A sample (290 cc.) of the product was introduced into the system, and compressed air was introduced to an internal pressure of 210 lb. per sq. in. After maintaining the system at a temperature of 260 C(500 F) for a period of 4 hr., it was allowed to cool. The gases were then removed and analyzed by methods described under "Analytical Tests of Products of Decomposition". No test for phosgene was made. The sample of the lubricant was removed, and its acidity and flash point determined according to the methods given under "Identification and Analytical Tests".

RESULTS

The results are given in detail in Table II below:

TABLE II

Test Temperature	260 C(500 F)
Time, hr., to reach test temp.	0.9
Initial air pressure, lb. per sq. in.	210
Air pressure 4 hr. after its introduction (or at the time furnace was turned off), lb. per sq. in.	210
Air pressure, furnace cool, lb. per sq.in.	195
Temperature variation during 4 hr. of test	± 3 C(5 F)
Properties of oil removed from system after test.	
Appearance	Slightly darker, frothed on removal
Flash point	202 C(395 F)
Acidity (per cent by weight HCl)	0.0075
Gas analysis	
Per cent CO_2	0.0
" " O_2	20.2
" " CO	0.0
" " CH_4	0.2
" " HCl	none
" " Cl_2	none

RECORD IN SERVICE

The product is in process of development and has not been in general use. Accordingly, data as to its record in service are not available.

THE SUBMITTOR

The manufacturer, the Swann Chemical Company of New York, is a division of the Swann Corporation and is submitting first product to us. This concern is well known in the chemical industry.

SUPERVISION OF PRODUCT BY THE LABORATORIES:

The product will be placed under Reexamination Service.

C O N C L U S I O N S

GENERAL NATURE:

This product is a mixture of chlorinated hydrocarbons, made in varying degrees of viscosity.

In Identification Tests it was found to exhibit the characteristics of hydrocarbons and to contain chlorine in the amounts stated by the manufacturer.

FIRE AND TOXIC HAZARD:

The product is practically nonflammable at ordinary temperatures. It is capable of forming moderately combustible and explosive mixtures with air under laboratory test conditions at higher temperatures, beginning at a temperature level somewhere within the range 318 to 331 F, but under practical conditions formation of combustible or explosive mixtures at temperatures as low as 331 F is regarded as extremely unlikely. The fire hazard is very small, being in a class only slightly greater than that of chloroform.

The gases or fumes produced by burning or decomposition of the product by heat include hydrochloric acid, carbon monoxide, and a small amount of free chlorine. This will ordinarily constitute a toxic hazard only where the conditions are such as to cause

confinement of the fumes, as in a closed room in which combustion or decomposition of the product is maintained by fire or highly heated surface. It is to be noted in this connection that oils in common use at present for the lubrication of steam turbines are readily combustible and, when burning under conditions of restricted air supply, form carbon monoxide in dangerous concentrations.

By reference to the results of Identification Tests, it will be noted that the flash point of the product is comparatively high, 201.5 C(395 F), and that a so-called "fire point" was not obtained. While intermittent flashes occurred in this test, the product did not continue to burn. The flash point and so-called "fire point" tests, particularly the latter, in the case of chlorinated hydrocarbons are of limited value as a measure of fire hazard but are useful for purposes of identification. The practical significance of the above tests in the case of the product in question is that its fire hazard is of a low order.

By reference to Explosibility of Vapors Test and Explosive Range Tests, it will be noted that vapors of the product failed to ignite or explode in tests at 159 C(318 F) but weak combustion occurred in tests at 166 C(331 F). In tests at still higher temperatures moderate explosions were obtained. At a temperature of 400 C(752 F), the explosive range of the vapor with air was found to be from about 1.2 to about 3.2 per cent by volume of vapor in air. It will be noted that this is a comparatively narrow explosive range.

As shown under "Ignition Temperature Tests", the ignition temperature of the product was found to be 642 C(1188 F) in an iron flask heated by a solder bath and 770 C(1418 F) when dropped upon a heated iron plate.

Hydrochloric acid, carbon monoxide, and a small amount of chlorine were found in the gases produced by decomposition or combustion of the product, as shown under "Results of Analytical Tests of Products of Decomposition". An all-service gas mask offers protection from these gases if formed in toxic concentrations in a confined space due to unusual conditions.

It will be noted that combustion and decomposition of the product was maintained by heated surfaces (459 C, 858 F) or by a gas flame in carrying out the Analytical Tests of Decomposition Products (see Tests 1 and 2). As shown by the results of the Decomposition Temperature Tests, appreciable decomposition did not occur at temperatures below 400 C(752 F).

STABILITY:

The product is reasonably stable and in use is unlikely to undergo decomposition resulting in an increase in fire hazard.

In the Decomposition Temperature Tests the product did not undergo appreciable decomposition at temperatures below 400 C(752 F). In the Decomposition Test at Elevated Temperature and Pressure (500 F, 200 lb. per sq. in.), the amount of decomposition was extremely small. Considerations of the chemical structure and properties of the product also indicate that it is reasonably stable.

UNIFORMITY:

It is judged that the uniformity of the product can be controlled within the limits covered by this investigation.

A consideration of the composition of the product and the general process of manufacture indicates that it would be practicable to produce the product in accordance with the standard established by the samples submitted.

R E C O M M E N D A T I O N

TO THE FIRE COUNCIL OF UNDERWRITERS' LABORATORIES:

We recommend promulgation of the following notice to subscribers and the action indicated thereby:

Guide No. 540 I12 February 3, 1934 - Laboratories' File MH2498

Swann Chemical Co., Mfr.,
1239 Graybar Bldg., New York, N. Y.

Lubricant

A synthetic oil intended for use as a general lubricant and particularly for the lubrication of steam turbines.

Marking: "Swanco", 80 to 150, stenciled on containers.

Listed by Report - An investigation of this product has been made by Underwriters' Laboratories, the results of which are contained in a report dated February 3, 1934, copy of which may be obtained either from the manufacturer or from the Laboratories.

Listed - Reexamination Service.

See description of Reexamination Service on guide card.

Tests by:	Report by:	Reviewed by:
A. F. Matson C. C. Clogston	C. C. Clogston Physical Chemist	Asso. Chem. Engr.

SUBMITTED

Chemical Engineer.

The foregoing Recommendation has been accepted

6 1934

UNDERWRITERS' LABORATORIES

(SIGNED) D. B. ANDERSON

Secretary

CCC:BIS

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