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T.A.C. REPORT LMC-1

(T.O.M. REPORT No. 13)

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J10A

SYNTHETIC LUBRICATING OILS FROM TETRAHYDRO-
FURAN, ADDITIVE FOR BREAK-IN OIL AND RECOIL
FLUID AT I.G. FARBENINDUSTRIE - LEVERKUSEN,
GERMANY

Handwritten signature
CHAS

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to the

TECHNICAL ADVISORY COMMITTEE

(A Subcommittee for the Technical Committee)

of the

PETROLEUM INDUSTRY WAR COUNCIL

July 25, 1945

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Report on

I.G. FARBENINDUSTRIE - LEVERKUSEN, GERMANY

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on behalf of the

British Ministry of Fuel and Power

and

U.S. Technical Industrial Intelligence Committee

C.I.O.S.

Target No. 30/Opportunity
Fuels and Lubricants

July 25, 1945

COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
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RECOIL FLUID

Summary

The mixture of triglycol, ethylene glycol and water used regularly by the German Army as recoil fluid was found unsuitable in the winter campaign in Russia. The addition of a sulfonamide of low molecular weight eliminated the difficulty since, in this way, it was possible to obtain a recoil fluid of not too high viscosity at low temperatures and still to maintain the high specific gravity necessary for satisfactory brake action.

Information was obtained by interrogating Dr. Detlef Delfs, on July 5 and 6, 1945.

Details of Formulation.

The composition of the German recoil fluids is given in the following tables. The addition of K_2F_2 prevents corrosion of light-metal alloys, whereas mercaptobenzo-thiazol was added for rust prevention. The mixture of sodium and potassium salts of phenylglycine served as anti-oxidant. The code name "methanamid" is used at Leverkusen for the monomethylamide of methane-sulfonic acid, $CH_3SO_2NHCH_3$, whereas "Sulfoathan" stands for the methyl-hydroxyethylamide of methane-sulfonic acid, $CH_3SO_2N(CH_2CH_2OH)$. The figures in the table give the composition as per cent by weight.

COMPOSITION OF RECOIL FLUID

	<u>Bremsflüssig-</u>	<u>Bremsflüssig-</u>	<u>Bremsflüssigkeit</u>	
	<u>keit</u>	<u>keit</u>	<u>Braun</u>	<u>Ark</u>
	<u>Braun</u>	<u>Ark*</u>	<u>Up to</u>	<u>Since</u>
	<u>(old formula)</u>		<u>1944</u>	<u>1944</u>
Triglycol	34	-	17	17.3
Ethylene glycol	34	51	42.5	42.3
Methanamid	-	5.0	2.5	3.0
Sulfoathan	-	8	4.0	3.5
Water	28	32	30.0	31.4
K_2F_2	2	2	2	-
Mixed Na and K) salts of phenyl-) glycine.)	1.9	1.9	1.9	-

*See page 2.

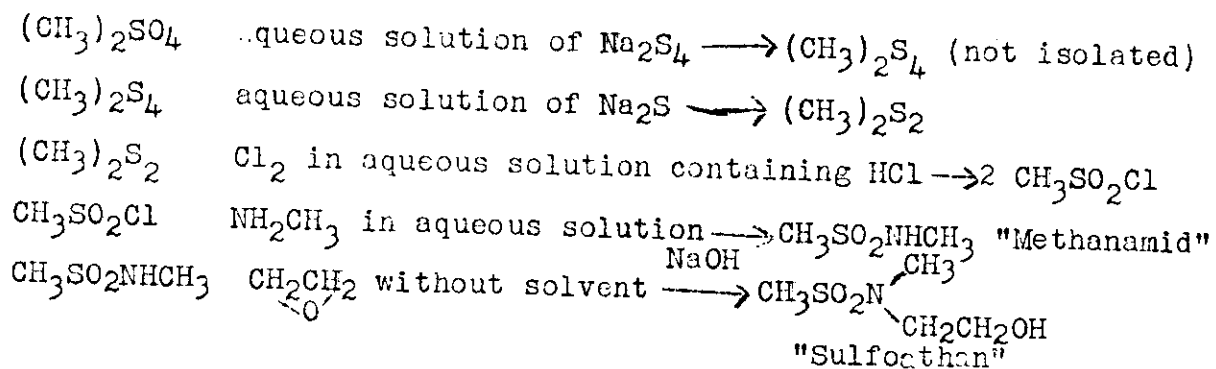
COMPOSITION OF RECOIL FLUID (cont)

	<u>Bremsflüssig-</u> <u>keit</u> Braun (old Formula)	<u>Bremsflüssig-</u> <u>keit</u> Ark*	<u>Bremsflüssigkeit</u>	
			Braun <u>Up to</u> <u>1944</u>	Ark <u>Since</u> <u>1944</u>
Mercaptobenzo- thiazol NaOh	0.1 -	0.1 -	0.1 -	- 2.0

*Formulated tentatively to save triglycol.

Manufacture of sulfonamide.

The manufacture of "Methanamid" and "Sulfoathan" is carried out according to the following scheme:



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H. Schindler.

SYNTHETIC LUBRICATING OILS FROM TETRAHYDROFURANSummary.

Synthetic oils of good viscosity index but poor thermal stability have been prepared at Leverkusen by copolymerization of tetrahydrofuran and ethylene oxide in the presence of FeCl_3 and SOCl_2 . Engine tests with an oil of a viscosity of about 33 SUS at 210°F . resulted in ring sticking after short running time and indicated that the piston was not properly lubricated, probably because of decomposition of the lubricant. The synthetic product is not miscible with petroleum oil. It has been used as gear oil and for the lubrication of machinery operating at temperatures below 280°C . Production of the material was irregular and on a small scale (maximum 1-2 tons a month).

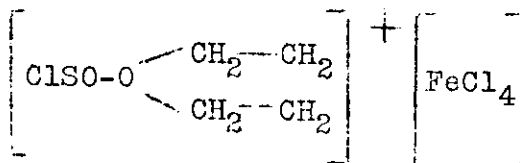
Information on the subject was obtained by interrogation of Dr. Otto Bohme, manager of the dyestuff intermediates department, and especially Dr. Detlef Delfs, head of the research laboratory of the intermediates department, on July 5 and 6, 1945.

Theory of Polymerization of Tetrahydrofuran.

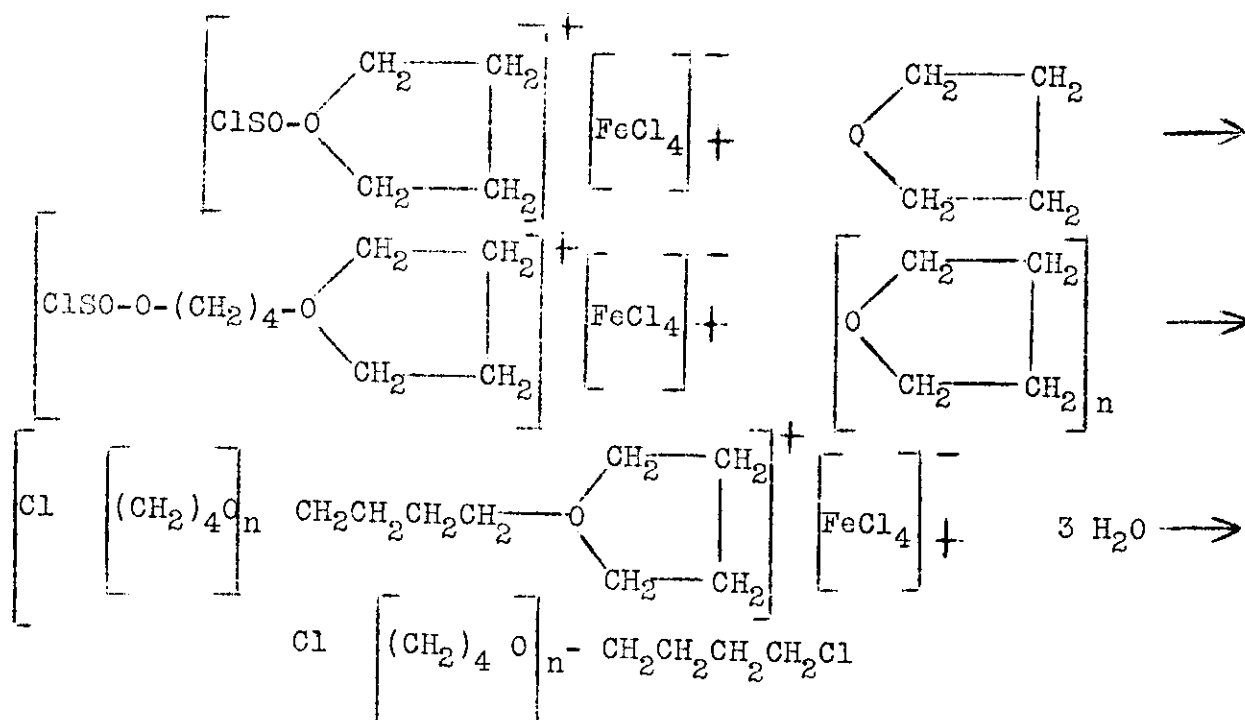
The ability of tetrahydrofuran to polymerize in the presence of oxonium salts was discovered by H. Meerwein and his collaborators, and the possibilities of the reaction were investigated by the I.G. at Leverkusen. A comprehensive patent application by the I.G. covering the present state of the chemistry of this field has been obtained.

The oxonium salt which serves as catalyst is formed directly in the reaction mixture from tetrahydrofuran, SOCl_2 and FeCl_3 . Other catalyst combinations are mentioned in the patent application.

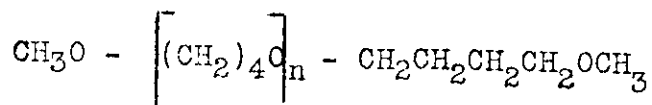
Reaction of tetrahydrofuran, SOCl_2 and FeCl_3 leads to the formation of a tertiary oxonium salt of the following structure:



This compound reacts with tetrahydrofuran according to the following scheme:



To eliminate the chlorine present in the molecule, the polymerizate is reacted with methanol to give the final product that has the following structure:



The above compound is a solid and is not suitable as a lubricant. In order to obtain liquid products, copolymerization with ethylene oxide or a similar compound is necessary. Copolymerization with propylene oxide, e.g., leads to synthetic oils with a pour-point of -60°C . Instead of methanol, it is of course possible to use other compounds; e.g., phenol.

Manufacturing Details.

Two grades of oil, M620, about 83 SUS at 210°F ., and M586, about 256 at 210°F ., have been prepared on the semi-plant scale. The manufacture of M586 was abandoned.

The catalyst can be prepared separately from tetrahydrofuran, FeCl_3 and SOCl_2 , which makes it possible to

operate the polymerization process continuously. Additional thionyl chloride is added in that case together with the reactants.

For the manufacture of M620, the molar ratio of tetrahydrofuran to ethylene oxide is 2:1 and the catalyst requirements are 0.1 mol FeCl_3 per 100 mols reactants and 5 mols SOCl_2 per 100 mols reactants. The polymerization temperature is 25-35°C. The polymerizate is left standing for several hours; the FeCl_3 is washed out with water, and water and unreacted tetrahydrofuran are removed by distillation. Chlorine is removed by reaction with methanol and NaOH at 90-100° in a closed vessel; excess methanol is distilled off; the mixture is neutralized with HCl and the NaCl formed is washed out. After the addition of 0.5% by weight of iso-octylphenol (as stabilizer), the product is dried and filtered.

The ratio of tetrahydrofuran to ethylene oxide is 4:1 for the manufacture of M586. The catalyst requirements are 0.1 mol FeCl_3 per 100 mols of reactants, and 2.5 mol SOCl_2 per 100 mols of reactants. The polymerization temperature in this case is about 25-30 C. The polymerizate is left standing for several days and neutralized (Congo Red) with NaOH. The unreacted tetrahydrofuran is distilled off, phenol and caustic are added to the polymerizate and the mixture is heated to 165°C. until no organic chlorine can be detected. The reaction product is then treated with water and neutralized with HCl. After the addition of 0.3% by weight (calculated on finished product) of isooctylphenol, the water is removed by distillation, the product is diluted with naphtha, filtered and freed from the solvent.

Inspection Data of Synthetic Oils.

Inspection data of the synthetic oils from copolymerization of tetrahydrofuran and ethylene oxide are given as follows:

<u>Oil</u> <u>Grade</u>	$d_{\frac{20}{4}}$	<u>Pour</u> <u>°C</u>	<u>Kinematic Viscosity (c stokes)</u>						<u>Pole Height</u>
			20°C	50°C	80°C	99°	150°	200°	
M620	1.024	-25	16.4	25.4	62	221		1.1	
M586	1.014		1032	244		55.3	22.4 11.2	1.1	

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	<u>% Chlorine</u>	<u>Conradson Carb.Res.</u>	<u>Flash</u> °C	<u>% Ash</u>	<u>Noack Evap.</u> <u>Test</u> (1 hr, 230°C, 20 mm.Hg)
M620	0.02	0.2	262	0.07	3.3%

Both oils are not miscible with paraffin hydrocarbons, but are soluble in alcohols, ethers, ketones, esters and aromatic hydrocarbons.

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H. Schindler.

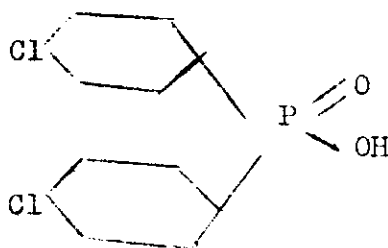
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ADDITIVE FOR BREAK-IN OIL

Summary

An additive for the lubricating oil used during the break-in period of engines, mainly aircraft engines, has been developed at Leverkusen. By the use of the additive it was possible to reduce the break-in time of German aircraft motors from 70 hours to 20 hours and to eliminate rejects.

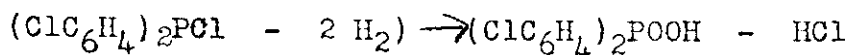
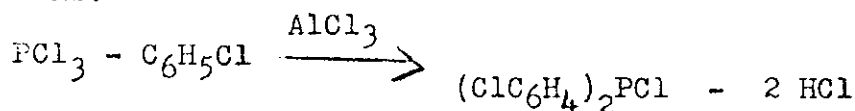
The effective compound in the additive is dichlorodiphenylphosphorous acid ("Product 891")



To increase the solubility in oil, the compound is used in the form of its stearylamine salt and to further increase ease of handling the additive was distributed as a solution in alcohol-benzol (50:50). The solution which contains 50% by weight of the stearylamine salt of Product 891 was termed J7. The break-in oil for aircraft engines consisted of Rotring Oil (RedBank) with 2% by weight of J7. The information was obtained by interrogation of Dr. Berthold Wenk, manager of the dyestuff department, on July 5 and 6, 1945.

Preparation.

The preparation of the additive is based on the following reactions:



To 1240 kg. of chlorobenzene and 760 kg. of PCl_3 is added, with stirring, 372 kg. of AlCl_3 . Since no reaction takes place in the cold, the temperature is rapidly brought to

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70-75°C. Development of HCl begins, and heating is continued according to the following schedule:

In 2 hours to 80-90°C.
" 2 " " 100-105°C.
" 4 " " 107-109°C.
" 4 " " 110-112°C.
" 4 " " 113-116°C.
" 4 " " 117-120°C.
" 4 " " 121-124°C.
" 6 " " 125-127°C.
" 6 " " 128-131°C.
" 8 " " 132-134°C.
" 28 " " 134-136°C.

Total 72 hours

Excess PCl_3 and some chlorobenzene are distilled off at atmospheric pressure until no PCl_3 can be detected in the overhead product; the residue is cooled to 70°C. and distilled under vacuum at 81-136°C during 7-8 hours. Of the chlorobenzene charged, about 800 kg. is used in the reaction and 400 kg. is recovered. The distillation residue is cooled to 50-55°C. and passed by N_2 pressure into 2000 liters of water and 2,500 kg. of ice. The yield of the crude moist product "Product 891" is 1200-1250 kg.

The following procedure is used for the purification of the crude product.

1200-1250 kg. of Product 891 is pasted with about 4000 liters of water, brought to the boiling point with direct steam, made weakly alkaline (phenolphthaleine) by the slow addition of about 250-300 kg. of Na_2CO_3 and boiled with direct steam for about 20 hours. The solution, whose volume is now about 7000 liters, is treated with about 250-300 kg. of concentrated HCl (technical) until it is barely alkaline (Brilliant Yellow indicator) and is then filtered at about 90-95°C. The residue is again pasted with 3000 liters of water, made alkaline (phenolphthaleine) with about 60 kg. of Na_2CO_3 , boiled for 6 hours, treated with about 40 kg. of HCl (weak indication of brilliant-yellow paper) and filtered. The filtrates of the two treatments are combined and acidified in portions of 1500 liters (strong Congo Red) with HCl; the reaction is carried out in an enamelled vessel of 2500 liter capacity. The total consumption of HCl is about 400 kg. Product 891 separates out as a viscous oil, which settles to the bottom of the vessel and the supernatant solution is drawn off.

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If the product still does not give a clear solution in a Na_2CO_3 solution, it is necessary to repeat the soda treatment. The total product obtained is dissolved in about 1000 liters of water, together with about 40-50 kg. of Na_2CO_3 (weakly alkaline towards phenolphthalein), boiled for 1/2 hour, made weakly alkaline toward Brilliant Yellow by means of HCl and filtered; the solution is again acidified in an enamelled vessel. The separated oil is repeatedly washed with water at 50-60°C. and the product is finally dried under vacuum at 135-140°C. Yield: 500-550 kg. of pure Product 891.

The preparation of the stearylamine salt and solution of the salt in alcohol and benzol is carried out in one step as follows: 800 kg. of pure Product 891 is heated to 60°C., 500 kg. of benzol is added with stirring and after complete solution 500 kg. of alcohol (94%) is added. The temperature has sunk to 40°C. by this time, and 200 kg. of stearylamine (well broken up) is added within about 1 hour. The temperature is maintained at 40-45°C. by cooling during this period. After complete solution has taken place, stirring is continued at 40-45°C. for 2 hours. The solution is allowed to stand undisturbed for 24 hours and is then filled into glass containers. Yield: 2000 kg. of J7.

Iron drums as well as galvanized or lead lined drums are not suitable for shipping the product.

Specifications for J7.

The following specifications have been proposed by the I.G. Leverkusen for the additive J7 for use by the German Air Force:

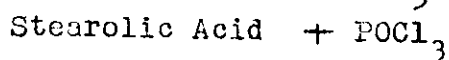
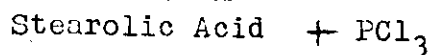
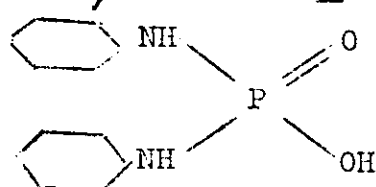
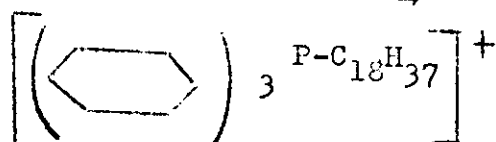
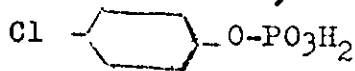
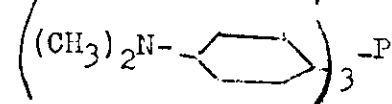
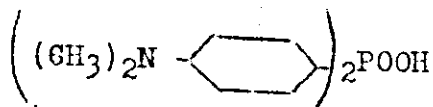
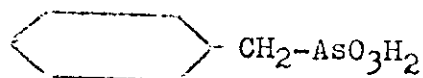
- | | |
|--|---|
| 1) Density $\frac{20}{4}$ | 1.004 - 1.015 |
| 2) Refractive Index $N_{\frac{20}{D}}$ | 1.491 - 1.494 |
| 3) Phosphorus content | 4.5 - 5.0% |
| 4) Solubility | A 2% solution in Redring (Red band) oil must show no residue and no separation must take place on cooling to 17°C. Opalescence on cooling is permissible. |
| 5) Performance | Rotring oil containing 2% J7 when tested on the Wieland Machine shall give no seizure at a load of 1500 kg. |

6) Identification of
J7

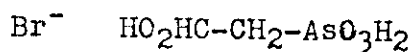
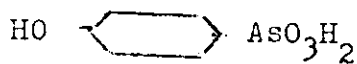
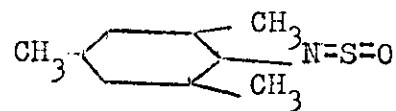
A red color appears
when 5 cc. of J7 are
mixed with 5 cc. of a
solution of 0.5 g. of
chloranil in 100 cc.
of odichlorobenzine.

Development Work.

In the course of the laboratory work to find
a suitable additive for break-in oil, the following
compounds were tested and found unsuitable:



- | | | |
|------|-------------------------------------|-------------------|
| 1.) | Diphenylphosphinic Acid | |
| 2.) | " | --N - propylamide |
| 3.) | " | N - propylamine |
| 4.) | " | - N - butylamine |
| 5.) | " | - Triethanolamine |
| 6.) | " | - Stearylamine |
| 7.) | " | - N - butylamide |
| 8.) | Dinitrodiphenylphosphinic acid | - dodecylamine |
| 9.) | " | - paraffinamine |
| 10.) | " | - Stearylamine |
| 11.) | Bis - (2-Chlorphenylphosphinic Acid | - Stearylamine |



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