

entire contents of this autoclave are put through a filter press and the filtered oil is stored prior to distillation.

The $AlCl_3$ complex recovered by centrifuging is decomposed in batches by the addition of water. Any oil separating in this process can be either treated and fractionated with the main oil stream or recovered separately.

The filter cake from the filter presses can be extracted with the light oil fraction from the process for additional heavy oil recovery, either by washing in-situ or subsequently in batch autoclaves. The total extract oil can be recombined with the main oil stream before the filter presses.

The gas liberated from the purging and venting of the polymerization autoclaves and from the centrifuges and adjacent receivers is water washed, caustic washed and its ethylene content recovered.

All vessels using methanol are provided with methanol reflux systems, after which the gases still vented are water washed before being discarded. The wash water is saved for methanol recovery.

10) Oil Fractionation:

The combined oil from the filter presses is steam distilled at atmospheric pressure to remove about fifteen per cent light ends. These light oils are used in making up catalyst slurry in the polymerization reactors.

The product from the base of the still is batch treated with about 2.5% of a natural Fuller's earth (from near Munich) at $158^\circ F$, filtered through presses to give the finished oil.

In some cases lime and silica gel are used in the final treatment instead of Fuller's earth.

OPERATING REQUIREMENTS

Utilities: The following utility requirements for the Leuna plant were given, based on one barrel of finished lubricating oil:

	Ethane Cracking & Ethylene Purification	Polymerization & Refining
H.P. Steam (220 psi), pounds	1080	430
L.P. Steam (22 psi), pounds	650	1950
Water (from River- Once-through)		
Winter ($40-50^\circ F$), gallons	11200	3700
Summer ($86^\circ F$), gallons	22400	3700
Nitrogen, Cubic Feet	-----1,350-----	
Electricity, KWH	450	160
Fuel Gas (250 BTU/CF, lower heating value), BTU.	1.51×10^6	0.10×10^6

Operators: The following operating personnel was required for the plant. These figures are based on a 56-hour week, or 3 men per job for 24-hour operation. They do not include any maintenance labour.

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	Total		Per Shift	
	Operators	Foremen	Operators	Foremen
Ethane Cracking	18	3	6	1
Ethylene Purification	87	3	29	1
Polymerization & catalyst separation	68)	6	23)	2
Distillation	12)		4)	
Final refining of lubricating oil	10		10 (Days only)	-
General Plant Foreman (Gericke)	-	1	-	1 (Days only)
Laboratory	7	1	2	1
Total:		Day Shift: 74	6	
	202	14		
		Night Shift: 64	4	

The total of 105 operators in the ethane cracking and purification plant might be reduced to 80 if more skilled operators were available.

Normally the plant is shut down for inspection for a 3-day period every 60 - 120 days. To come on stream from a complete shut-down requires about two weeks.

TESTS ON PRODUCTS

As indicated above, the plant could be operated to produce either a 6° or a 3° Engler viscosity oil (at 100°C). These products from Leuna were referred to as SS (Schmierstoff) 906 and 903 respectively and specifications for the products were as follows:

	SS.906	SS.903
Specific Gravity at 20°C Max. (API at 60°F. Min.)	0.862	0.860
Viscosity at 50°C (Engler)	31.9	32.3
" " 100°C (Engler)	44-46	14-15
(SSU at 150°F)	5.63(Min)	3.0(Max)
(SSU at 210°F)	1200-1250	400-440
Viscosity Index. Min.	205(Min)	105(Max)
Slope constant "M" in Pole Height Calc., Max.	107	115
Pole Height, Max.	3.05	3.20
Pour Point °F, Max.	1.73	1.60
Flash Point, °F, Min.	-13	-31
Neutralization No. (mg KOH/g), Max.	435	392
Saponification No., Max.	0.06	-
Moack Evaporation Test (482°F) Max. %	0.30	-
Conradson Carbon Residue, Max.	8	-
Sh, Asphalt, Water	0.2	0.2
	0	-

The SS 906 product was usually blended with an equal quantity of bright-stock derived from petroleum oil, the blend being used as an aviation lubricating oil (denoted S-3).

The natural lubricating oils used in the blend were from three sources all from refining Austrian crudes, and were denoted as follows:

- 607 - From Rhenania, Harburg. Vacuum distilled oil, refined with sulphuric acid.
- 707 - From Vacuum Oil Co., near Bremen. Duo-Sol refined.
- 807 - From Norag, near Hanover, Furfural refined.

Alternate stocks to the SS 906 (Leuna) product in this S-3 blend were the following:

- SS 1106 - 6°Engler (100°C) oil by polymerization at Politz of olefines obtained by cracking paraffin.
- SS 1006 - 6°Engler (100°C) oil by polymerization at Rhenania, Harburg, of olefines obtained by cracking paraffin.
- SS 906 - 6°Engler (100°C) oil by polymerization at Schkopau of ethylene produced, via acetylene, from calcium carbide.

The specification for the S-3 blended aviation lubricating oil is given below:

Viscosity, Min. 2.8° Engler at 100°C (98 SSU at 210°F).	
Viscosity Index, Min.	95
Flash, F., Minimum	428
Pour Point, Maximum	-4
Conradson Carbon Residue, Max.	0.3

A 3° Engler (100°C) oil from Politz (SS 1103 was sometimes used directly. Maximum production of this grade was 200 Tc/yr (4 B/D).

A standard engine test was used for the determination of the ring-sticking tendencies of aviation lubricating oils. As a reference oil, a refined petroleum lubricant (Vacuum Oil Co. "Rotring") was used, and results were reported in terms of hours operation before ring-sticking. The various oils described above compared as follows:

Reference oil (Rotring)	8 hours
Synthetic oil (Leuna) 100 SSU/210 (SS 903)	32 hours
" " (Politz) " (SS 1103)	20-22 hours
Finished Blend (S-3)	12 hours
" " " plus 0.2% Inhibitor "R"	16 hours

PRODUCTION DATA

Total German production of synthetic aviation lubricating oil was as follows:

	Design		Actual Production	
	Metric		Metric	
	Tons/Mo	B/D	Tons/Mo	B/D
Leuna	850	206	700	170
Schkopau	350-500	85-121	350-500	85-121
Politz	1200	290	1000	242
Rhenania, Harburg	700	170	500	121
Total (Max.)	3250	787	2700	654

This production had been reduced by bombing as follows:

Leuna - No production after July-August 1944 because of lack of ethane after bombing of hydrogenation plant.

In later raids the lubricating oil plant itself was damaged. The vessels and pipe line of the cracking section were badly pierced by bomb splinters but the cracked gas purification plant was not too badly damaged. The Linde refrigeration plant compressor house was wrecked but possibly 50% of the compressor capacity could be salvaged. The polymerisation and distillation sections appeared more or less intact but storage tanks and general service piping in the area were very badly damaged.

Pöhlitz - Production reduced to 500-600 T/Mo. in last 6 months' operation.

Rhenania - No production after July 1944 bombing. Plant was planned to be moved to Harz Mountains but was not completed there.

An ultimate total production capacity of 70,000-80,000 Tons/yr (1410-1610 B/D) synthetic lubricating oil was planned and plants had been erected at Moosbierbaum and Blechhammer, but never operated.

NOTES ON CATALYSTS AND REACTION CONDITIONS

1) Acetylene Removal Catalyst

The catalyst (Kontakt 4788) is manufactured as follows:

Fifty kg. (110 lbs) chromic acid, 9.24 kg. (20.6 lbs) nickel nitrate, and 20 litres (5.3 U.S. gal.) water are mixed in a stainless steel vessel. The vessel is gas-fired, and the mixture is hand-stirred for several hours until it gives a thick black mixture with no more evolution of nitrogen-gases. This mixture is heated 12 hours at 572°F in an electric-heated furnace. After cooling, the resultant hard cake is broken by hand into 3/8" (8-10mm) granules.

The granulated mass is placed in an electrically-heated reduction oven, heated in an atmosphere of nitrogen to 842°F and held at this temperature for eight hours in the presence of hydrogen. The catalyst is cooled in a stream of hydrogen and stored in containers in a nitrogen atmosphere.

The composition of the finished catalyst is approximately 95% chromic oxide and 5% nickel.

2) Ethylene Purity Required

For ethylene polymerization, the following limitations on ethylene purity must be observed:

Carbon dioxide - Complete absence, no trace with barium hydroxide test.

Oxygen	- Complete absence, reactor must be purged with ethylene before starting operations.
Hydrogen Sulphide	- Complete absence.
Carbonyl Sulphide	- Complete absence.
Mercaptans	- Complete absence.
Thiophenes	- Complete absence.
Carbon Monoxide	- Maximum 0.005%. Check with standard haemoglobin solution, followed by spectroscopic determination of the width of the absorption band.
Hydrogen, methane, ethane, acetylene	Total must not exceed 5%

3) Polymerization Catalyst

Pure aluminum chloride is unsuitable as a polymerization catalyst because it is too active and permits too many side reactions, including isomerization and cracking. It is modified to a suitable form by the addition of about 4% by weight of ferric chloride. The catalyst is prepared at Ludwigshafen and Schkipau by treatment with carbon monoxide and chlorine of a natural bauxite which contains about the correct amount of iron oxide. Any traces of titanium, silicon, or magnesium chlorides present in the finished catalyst do not seem to affect its polymerizing qualities.

The maximum temperature reached during formation of the catalyst complex with ethylene in the presence of light oil controls the activity of the catalyst and the type of oil subsequently produced. The higher this maximum temperature the higher both the VI and the pour point of the product. A good compromise on these two tests calls for a maximum temperature of 356°F.

As previously mentioned, the polymerization temperature governs the viscosity of the final product. According to Zorn, an oil of 6° Engler at 100°C (220 SSU at 210°F) is produced at 212-230°F and an oil of 3° Engler at 100°C (105 SSU at 210°F) at 266-284°F. These temperatures are lower than those already reported for Leuna plant operation, probably because of a difference in ethylene purity between laboratory and plant operations.

Other catalysts have been tried for ethylene polymerization properties, but without much success. Aluminium chloride plus metallic aluminium is too strong a catalyst for the reaction and hydrofluoric acid tends to form ethyl fluoride instead of a polymer.

Boron trifluoride in HF can be used as a polymerization catalyst but produces an inferior quality of oil.

THEORY OF LUBRICATION

This subject was discussed in detail with Dr. Zorn at Leuna. His work in this field has been continuous since about 1927, and he is credited with the development of the commercial synthetic lubricating oil manufacture.

Preliminary research showed that an olefine to be used for polymerization to a high V.I. lubricating oil must have a double bond at the end of a straight

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chain molecule, with the exception that an iso-structure at the opposite end of the molecule from the double bond may give some advantage, as discussed later. No substitution may appear at the double bond.

For instance, the following examples of isomeric octene polymerization bring out the effect of differences of structure:

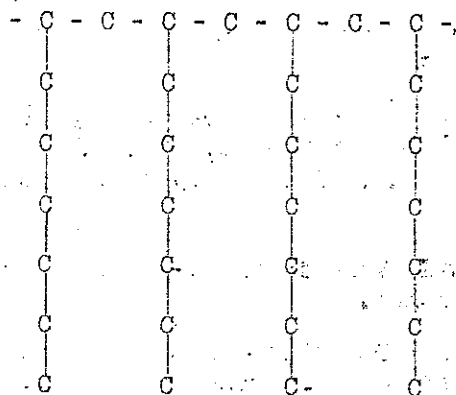
Olefine Feed	Polymerized Product					Yield wt. %
	Mol.wt. (Approx.)	Viscosity			V.I.	
		Engler at 100° C.	SSU at 210° F.			
n-octene-1	800	2.8	98	100	80	
2-methylheptene-1	350	1.2	32	20	20	
n-octene-4	200	0.8	28	-10	5-10	
6-methylheptene-1	1500-1700	7.9	290	100	85-90	

The theory based on these observations and some organic syntheses is as follows:

The ability of an oil to function as a lubricant involves a molecular structure which permits close approach of the chain carbon atoms and the metal surface so that dispersion forces between the atoms of the metal and the lubricant can become effective. For good viscosity characteristics, likewise, it is necessary that the molecules should have a structure which gives close contact of the individual molecules in order to utilize the dispersion forces active between molecules of the oil. As the magnitude of the dispersion forces increases, the viscosity index of the oil increases also, and more energy (heat) has to be added to overcome those forces and decrease the resistance to flow of the oil. This is a disadvantage insofar as the pour point of the oil increases when the viscosity index of the polymerized oil is increased. A compromise between these two properties must be made in practice by preparing an oil with a V.I. somewhat higher than that of petroleum oils and with a reasonably low pour point.

The relation between V.I. and pour point is demonstrated by the following examples:

(1) Octene-1 polymerized to this type of structure:

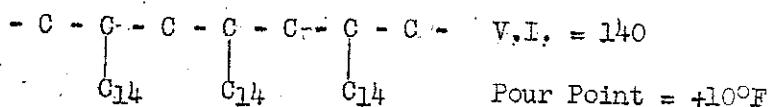


V.I. 110

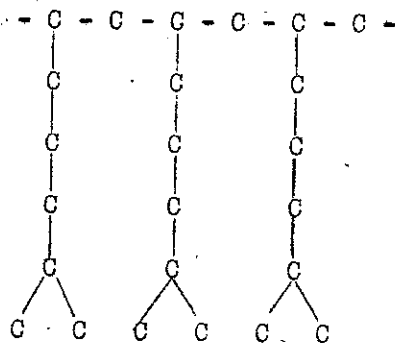
Pour Point -40°

This is approximately the structure which is obtained by ethylene polymerization at Leuna.

(2) Hexadecene - 1 polymerizes to this type of structure:

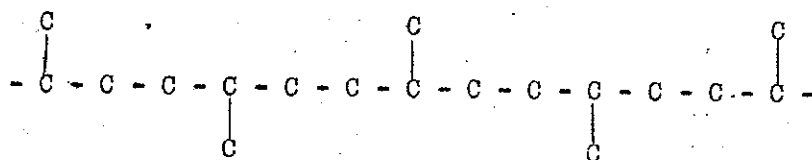


• Polymerization of a branched chain olefine like 6-Methylehptene-1 yields a product of the following structure:



In this case the viscosity of the oil is increased because additional forces become effective between the terminal methyl groups.

Isobutylene polymerizes to give a polymer of the following structure:



The location of carbon atoms on alternate sides of the straight chain prevents close contact between the carbon atoms in the main chain and the atoms of the metal to be lubricated. Consequently the isobutylene polymer cannot be used as a lubricant, in spite of its high V.I. (110-120) and satisfactory physical properties. Bearing failure results after a few hours when this oil is used in an engine.

Similar considerations apply in the case of propylene, which apparently forms chains through the centre carbon atom, thus giving side chains on both sides of the main chain. The V.I. of the polymer is about 85 and the polymer is unusually heat stable.

N-butylene with the double bond in the 1- position gives a good lubricating oil but butene -2 does not.

The change in dispersion forces between molecules is further illustrated by the change in melting point of hexadecane upon addition of methyl groups.

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	<u>Melting Point °F</u>
Hexadecane	+48
+ 1 CH ₃ group	-47
+ 2 CH ₃ groups	-126

Sources of Olefines:

Olefinic material suitable for polymerization has been obtained by cracking several types of wax. The wax must be of a straight-chain structure and must be cracked in the vapour phase with no liquid present. To obtain structures with the double bond at the end of the molecule, the cracking time must be short at high temperatures, forming at least 95% olefine, followed by a quench to prevent isomerization of the olefine and migration of the double bond.

Wax from the atmospheric pressure Fischer-Tropsch process without the heaviest ends (controlled by maximum melting point of 176°F) is a suitable cracking stock. Wax from the 20-atmosphere (300 psi) Fischer-Tropsch synthesis is unsuitable because of branched chain paraffins. Wax from brown coal tar distillation is suitable for production of the required type of olefine.

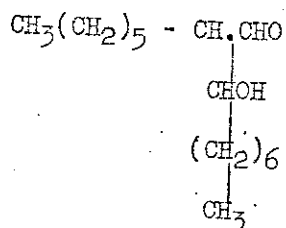
Petroleum wax as such cannot be easily handled by the above process, but can be converted to suitable wax by a combination cracking-hydrogenation step which yields a mixture of 50 per cent Diesel oil and 50 per cent straight chain paraffin wax. Hydrogenation is carried out at 3000 psi and 750°F with a tungsten sulphide catalyst and this process is in use at Ludwigshafen where 1000 tons per month slack wax from Hanover crude containing 60 per cent paraffin is processed.

The plant at Politz cracks a mixed wax containing Fischer-Tropsch wax, brown coal tar wax, and the special petroleum wax prepared at Ludwigshafen. A special process has been developed by Rhénania for direct utilization of petroleum wax.

Hydrocarbon Synthesis:

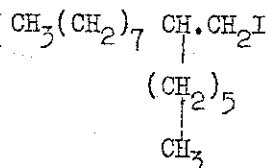
In the course of the study of the structure of lubricating oils, certain hydrocarbons were synthesised. The general method of synthesis is outlined as follows:

1. n-octyl alcohol was oxidized to the aldehyde.
2. An aldol condensation was carried out on the aldehyde to yield the following product:

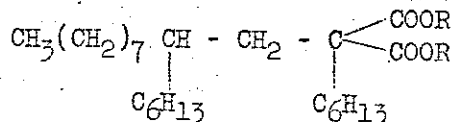


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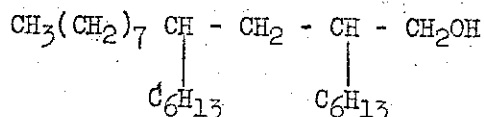
3. This product was reduced to the alcohol and converted into the iodide:



4. This compound was condensed with a suitably substituted malonic ester to give:



5. This product was reduced to give:



6. Steps 3 to 5 were repeated to add side chains and build compounds up to about 600 molecular weight.

LUBRICATING OIL ADDITIVES & SPECIAL PRODUCTS.

As the war progressed, it became necessary to develop lubricants, sometimes to augment dwindling supplies of otherwise satisfactory materials, but usually, as in the case of Machine Gun Oil, Recoil Oil, R.R. Axle Oil, and others, to secure improved products, usually with rust preventive properties. The development and manufacture of many of these new special materials was assigned to Dr. Zorn's laboratory at Leuna, on account of the wide experience available there on synthetic lubricating oil.

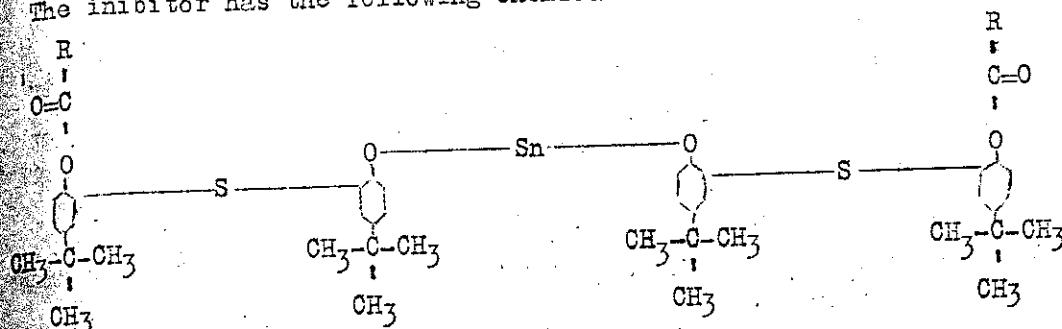
Special attention was given to compounds which could be made readily from materials already available at Leuna and two outstanding developments were Mesulfol 2, an extreme-pressure additive, and KSE, a rust preventive. Other important blending agents of the ester type were being manufactured for inclusion in special oils used by the German armed forces. Detailed information on the blending agents made at Leuna, the methods of preparation, properties and utilisation was obtained from Dr. Rössig and samples of the various products were obtained for assessment.

The individual additives are first dealt with and then the specialised lubricants incorporating these additives.

I Additives

(1) Inhibitor "R" (also known as "ZS-1") This inhibitor does not prevent oxidation of the oil, but guides the course of oxidation so that harmful ring-sticking products are not formed. The inhibitor has no effect on pour point, bearing corrosion, wear, or lubricating properties (Schmierfähigkeit)

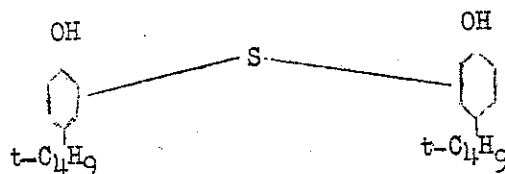
The inhibitor has the following chemical formula:



where R represents branched-chain hexyl, heptyl or octyl groups.

The steps in the synthesis of this inhibitor are as follows:-

- 1) Phenol is alkylated with isobutyl alcohol to give p-tert-butyl phenol.
- 2) P-tert-butyl phenol is treated with S_2Cl_2 to give the following compound:



- 3) This compound is treated with metallic sodium to make the corresponding sodium salt.
- 4) The acid chloride of the carboxylic acid to be used later in the esterification step is prepared by treating the acid with sulphuryl chloride. The carboxylic acids are manufactured from higher alcohols obtained as by-products during synthesis of isobutyl alcohol.
- 5) One mole of the product from step (3) is combined with one mole of the product from step 4 to esterify one phenolate group only.
- 6) This product is treated with stannous chloride in methanol to give the inhibitor as final product.

2.455. A mixture of the adipic esters of 140-180° C. alcohols obtained as by-products from isobutanol synthesis is prepared by heating to 160° C., a mixture of 1.6 g. alcohols, 0.48 g. adipic acid, and 0.0015 g. B-naphthalene phenonic acid. The reaction mixture is washed with a 20% NaOH solution and distilled under 0.2 mm. Hg. pressure until the still bottom temperature reaches 100° C. The material remaining in the still is then refined with CaO and Fuller's Earth.

2.504. A mixture of adipic esters of 160-200° C. alcohols ($C_8 - C_{12}$) from isobutanol synthesis. Three methods of preparation were obtained:
1. 1.7 g. alcohol mixture, 0.64 g. adipic acid and 0.0017 g. B-naphthalene phenonic acid are heated to 180° C.

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(b) Direct esterification of pure adipic acid, using 15% excess alcohols and 1.0 - 1.5% benzene sulphonic acid as catalyst at 150 - 160°C. (N.B. both (a) and (b) water distills off at 150 - 160°C and equilibrium is shifted towards completion of the desired reaction).

(c) If pure adipic acid is not available, the methyl ester of adipic acid is first prepared. After purification, the methyl ester is reacted with the alcohol fraction under similar conditions to (b). The last method was in general use at Leuna.

The reaction product is washed with 20% NaOH solution and the washed ester distilled at 0.2 mm. Hg. pressure until the overheads temperature reached 110°C. The liquid remaining in the still is refined with CaO and Fullers' Earth.

Physical properties of the ester are:

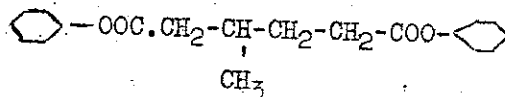
Pour Point - 94°F
Viscosity Index 135 - 155

Production of this ester at Leuna was about 20 tons/month. It was noted that straight chain alcohols did not give as satisfactory a product as the branched chain alcohols.

(4) E.515 Mixed adipic esters of 140-180° alcohols from isobutanol synthesis.

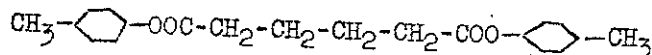
1.7 g. alcohol mixture, 0.42 g. adipic acid, 0.0017 g. β -naphthalene sulphonic acid are heated to 220-230°C and the reaction product washed with 20% NaOH solution. The washed ester is distilled at 0.2 mm. Hg. pressure until the overheads temperature reaches 135°C. The liquid remaining in the still is refined with Fullers' Earth.

(5) E.3022 The ester formed between cyclohexanol and 2-methyladipic acid.



1.5 g. cyclohexanol, 0.82 g. 2-methyladipic acid and 0.002 g. β -naphthalene sulphonic acid are heated to 170°C. The reaction product is washed with caustic soda and then water. Excess cyclohexanol is distilled off and the ester distilled at 0.2 mm. Hg. The distillate is stirred with 2% CaO plus 3% Fullers' Earth for 1 hour at 70°C to remove acid.

(6) E.3023 The adipic ester of p-methylcyclohexanol



prepared in a similar way to E.3022, from 1.5 g. p-methylcyclohexanol, 0.75 g. adipic acid and 0.002 g. β -naphthalene sulphonic acid.