

FILM STUDY GROUP
SUBJECT INDEX AND REPORT
T.O.M. REEL NO. 98
Prepared by
STANDARD OIL COMPANY (INDIANA)

TECHNICAL OIL MISSIONMICROFILM REEL 98SUBJECT INDEX

Prepared by Standard Oil Company (Indiana)

<u>Subject</u>	<u>Reel No.</u>	<u>Frame</u>
BEARING LUBRICANTS TESTS	98	80
DI-CHLOROPHENYL PHOSPHATE	98	51
DICRESYL PHOSPHATE	98	55
DI-NITROPHENYL PHOSPHATE	98	50
DIPHENYL PHOSPHATE	98	46
FILM STRENGTH IMPROVERS	98	14
LUBRICANT ADDITIVES	98	4
LUBRICANT TESTS	98	76
PHENYL PHOSPHINIC ACID DI-P-CHLOROPHENYL ESTER	98	43
PHENYL PHOSPHINIC ACID ESTERS	98	40
PHOSPHATES, ORGANIC	98	9
PHOSPHENYL CHLORIDE	98	10 41
PHOSPHINES	98	46
PHOSPHORUS ADDITIVES BIBLIOGRAPHY	98	114

<u>Subject</u>	<u>Reel No.</u>	<u>Frame</u>
PHOSPHORUS COMPOUNDS	98	4
--preparation	98	37
PHOSPHORUS SULFOCHLORIDE PREPARATION	98	62
RING STICKING TESTS	98	82
THIOPHOSPHATES	98	64

Microfilm Reel 98
(Original Designation Target SO/12.04)

TECHNICAL OIL MISSION
U.S. BUREAU OF MINES NO. 00 REEL NO. 2

Screened by Standard Oil Co. (Indiana)

Technische Hochschule (School of higher technical learning)
Stuttgart - Dissertation

The Preparation of Phosphorus Compounds and Their Use
in Lubricants

By Gerd Müller, Stuttgart

Date of Presentation, December 1, 1944

The following thesis deals with the synthesis of organic compounds containing phosphorus, their testing in oil testing devices for suitability as additives to lubricants, and their trial in practical motor experiments. The preparation and selection of the compounds were carried out at the Organisch-Chemischen Institut of the Technischen Hochschule Stuttgart under the guidance of Professor Dr. E. Ott. I owe him much gratitude for his constant help and support to my work.

Professor Glockner of the Institute for Metal Physics at the K.W.I. for metal research suggested the investigation. He also conducted the execution of the tests and trials. He made the progress of the investigation possible by merging (correlating) chemistry, physics, and machine construction at the University with the chemical and motor construction industries and the service stations of the Army into a working partnership. I thank him for his suggestions and advice that were always at my disposal. I thank particularly Dr. Brockstedt who showed great interest in the chemical side of the question. He aided me in consultations and through official experiments he made himself helpful. Also he put at my disposal a number of pictures. The necessary means were supplied within the scope of an order by the research station of the RdL (?) and ObdL (?). Extensive experiments were carried on in cooperation with the institute for metal physics at the K.W.I. for metal research, Stuttgart (Professor Glockner).*

* R. Glockner. Improvement of the bearing properties through lubricant admixtures. Berichte der Lilienthal Gesellschaft für Luftfahrt-Forschung 170/34 (Reports of the Lilienthal Society for Aviation Research).

The Staatl Material Prüfungs Anstalt (Public Institute for Material Testing) of the Technische Hochschule Stuttgart. (Dr. Brockstedt)**

The Research Institute for Heat Engines at the T. H. Stuttgart (Professor Wowerka, Dipl. Ing. Dollhopf, Dipl. Ing. Hagmayer),*** and the Daimler-Benz A. G. Stuttgart. Untertürkheim (Dipl. Ing. Anders). I have included part of the results in my thesis for better comprehension.

I. Introduction

Based on a series of experiments (149) published by an English author and with regard to some investigations that were carried out by Dr. H. C. Brockstedt on the State Institute for the Testing of Materials of the T. H. Stuttgart on compounds prepared by us, we first suspected that the addition of triphenyl-phosphine would give valuable properties to mineral oils. On the one hand it seemed to reduce the friction values and on the other hand the resistance to pressure of the oil film seemed to be considerably increased. In my diploma thesis it was proven that these properties were not caused by the admixture of triphenylphosphine itself but by the addition of monophenylphosphine. Since monophenylphosphine is easily oxidized in the air, it is not usable for practical purposes. Also phosphenylchloride, which is similarly constituted and was proven very effective in low concentration, is not mixed because of other properties such as low boiling point, easy decomposition by water and splitting off HCl.

The purpose of this investigation was to use this knowledge that was obtained and to develop preparations that would be suited (because of the rest of their properties) to improve lubricants of mineral oil basis.

First phosphenylic acid, which was already prepared during my diploma thesis, was studied more closely in spite of its poor solubility qualities. Since it is a direct derivative of phosphenylchloride, one could expect the same properties, improved friction value and resistance to pressure. Its effect corresponded to its configuration, some other properties were also favorable. But the decomposition into monophenylphosphine, benzol and metaphosphoric acid at stronger heating prevented the use in the combustion engine which was strived for particularly at first.

Following is a list of properties which are required of an admixture to the oil of highly strained combustion engines (airplane motors) besides its actual effect.

- (1) High temperature stability; if possible over 300°C.

** K. Wellinger and H.C. Brockstedt. Stability of the effect of chemical admixtures in experimental runs of airplane motors both single cylinder and complete engines. Experimentation report of January 5, 1944.

*** A. Wowerka. Basis and Results of the slide bearing tests. Berichte der Lilienthalgesellschaft für Luftfahrtforschung 170/38.

- (2) Oil solubility that makes it possible to add appropriate solution mediators.
- (3) Corrosion of the materials that are to be lubricated must be kept in low limits.
- (4) Resistance to water and leaded naphtha.
- (5) Cause no negative changes in the physical properties of the oil (viscosity, solidifying point, flash point, foam, etc.), or in the chemical lubricant tests (coking, aging, neutralization number, etc.).
- (6) Low toxicity.
- (7) Bearing resistance.
- (8) No increased ring sticking.
- (9) Easy synthesis and available starting materials.

As one can see from the great number of patents in this field, (particularly in the U.S.A.), the search after such a material is not easy. It becomes easier if one does not look for a universal admixture but rather limits the intended use somewhat. Then one can forego one or the other of the points mentioned above. Our interests were directed particularly to the running in process. There the corrosion of the bearing which occurred frequently required immediate remedy. Since the motors are taken apart again after running-in some of the requirements 1-9 are not so distinct. We also dealt with gear oils where the oil-bath temperatures are not as high. It is to be mentioned here also that the admixtures respond differently to changes in the combinations of work materials and in the oil, which complicates the selection.

In my search for a material which configuratively is similar to phosphenylic acid but considerably more resistant to temperature, I came upon Phenylphosphine acid diphenylester. This compound can be distilled at a boiling point 570-580°C, nearly without decomposition. It does not have a free OH group and its properties are different accordingly. I will report about these relations below. Because of the difficulties in preparing large amounts of the ester, we went back to substances of the phosphoric acid ester series that are constituted similarly but are more readily available. First diphenylphosphate and later diparahalogenphenylphosphate were studied. The effect was increased considerably by the introduction of the halogen in the para position. Sulfur derivatives were also used in the experimentation. The OH-group was reacted with an alcohol because the temperature resistance of these acid esters was not sufficient.

The surprisingly good values obtained at first with methyl ester could be explained later after the preparation of more easily dissolved propyl and lauryl ester (as attributable to) an impurity of monochloride. Diparachlorophenylphosphoric acid-monochloride is not stable at temperatures above 280°C. Then we produced phenylphosphinacid monophenylester-monochloride which is more heat-stable and which transforms in possible saponification into monophenyl ester which is also effective. For further improvement the phenolic nucleus was chlorinated in the para position. That preparation gave also usable results but caused a disagreeable resinification, which did not allow its use. Experiments with diparachlorophenylphosphoric acid-sulfochloride were carried out because sulfochlorides are generally considerably more resistant to water than oxychlorides. Thereby medium carrying capacities were obtained. An attempt will be made below to explain the connections between the various preparations. For sake of completeness I mention that I.G. has developed preparation 891 based on our investigation. According to their statements it is technically a chlorophenyl phenyl phosphoric acid. This preparation has been proven good and can be produced in practical quantity. It contains a free acid hydroxyl-group.

The justification to use particularly phosphorus compounds as basis for a thesis on high pressure lubricants became clearly apparent in the course of our investigations. Additions of other classes of materials be it fatty acid, sulfur or chlorine compounds which are mentioned in the literature as valuable were also tested by us and they gave unsatisfactory results. To be sure, these statements as well as those about the use of phosphor compounds cannot be compared directly with ours since they were gotten on different test apparatus. Nevertheless we have searched the literature for admixtures of phosphorus compounds, at the end of our thesis (see part 5). The phosphines which occupied us mostly during our diploma thesis comprise only a small part in the series of information, as do the phosphatides and inorganic compounds like P_4 , S_8 and $PHCl_2$. Considerably more space is devoted to esters of phosphoric acid and phosphorous acid. The information does not coincide with our control experiments. Neutral phosphates with or without sulfur in the molecule gave neither higher pressure resistance nor lower friction values. A summary of the substances used can be found further down.

Various explanations were given for the cause of the effect of such additions. Kern (150) puts the formation of metal phosphate layers into the foreground. Beeck, Givens and Smith (149) assume that the phosphorus of the corresponding combination is reduced and then forms low melting phosphides with the sliding surface. Therefore the latter prefer tri-valent phosphorus ~~in order to facilitate the reduction. Contrary to that we have found in our~~ investigations that particularly five valent phosphorus compounds have an excellent effectiveness. Other authors like Wolf, Kluge, Frowing, Donandt, Trillat (151-155) direct their attention primarily to the adsorption of the corresponding molecules to the metal surface caused by the polar groups. Several methods to measure the adsorption were worked out. Bachmann and Brieger (156) have measured the heat of adsorption of oils on metal powder. An adheroscope was developed in American that makes it possible to follow gravimetrically the amounts of oil adsorbed. Kadmer explains in a new investigation that he has not been able to determine any connection between dipole-moment and lubricant ability.

Accordingly, to our present results for phospho compounds we require of the additive molecule that they contain besides the atom also a very active group with the aid of which it is held tight to the sliding surface. Otherwise one could not explain the effect of such small amounts as 0.1%. But I do not consider these adsorptions to be the determining factor in the process. Rather, the reaction with the surface must occur at that time. This is the reason for the in some respects entirely different behavior when the material is varied, but also for the finest polished surfaces after the run (Fig. 21 + 22) as they were determined in the experiments of Daimler-Benz Co. The attack on the metal surface through HCl that was formed was too strong for some very aggressive materials (phosphenylchloride). Notably this compound shows no improved effect when used on silver bearings (AgCl!!). The other materials are able to polish or wear off the small points and prongs which are present even on the finest polished surfaces. Thereby the tearing of the lubricating film and in turn the corrosion of the metal parts is prevented. It is of interest in that respect that according to experiments of Professor Glocker the traces of processing disappear completely through electrolytic etching of ground steel sections with phosphoric acid-acetic acid anhydride.

The active group in phosphenylchloride consists of the two Cl atoms $\left(\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{P} \\ | \\ \text{C}_6\text{H}_5 \end{array} \right) \begin{array}{l} \text{Cl} \\ \text{Cl} \end{array}$ and in the phosphonic acid $\left(\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{P} \\ | \\ \text{C}_6\text{H}_5 \end{array} \right) \begin{array}{l} \text{OH} \\ \text{H} \end{array}$, and diphenylphosphate $\left(\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{P} \\ | \\ \text{C}_6\text{H}_5 \end{array} \right) \begin{array}{l} \text{O} \\ \text{O} \end{array}$ it is the acid OH groups. Also phenylphosphoric acid diphenyl acid contain the configuration $\begin{array}{c} \text{O} \\ || \\ \text{P} \\ | \\ \text{OH} \end{array}$ but here the OH group is etherified with phenol. In this connection it should be noted that the esterifying of the OH group in the diphenylphosphate injures the effectiveness. According to our experiences so far it is necessary that in addition to the two molecule parts (P and active group) there is as a third part at least one aryl or alkyl group. Otherwise phosphoric acid $\begin{array}{c} \text{HO} \\ | \\ \text{P} \\ | \\ \text{OH} \end{array} \begin{array}{l} \text{O} \\ \text{OH} \end{array}$ should show the effect also which it does not. The effect is increased through the introduction of a halogen into the nucleus. Thereby the para position was chosen primarily, since p-halogen phenols are easily prepared. Lincoln, Byrkit and Steiner (158) determined too that those compounds that take halogens in para position have greater influence on film strength. They used a Tinker machine and simple aromatic compounds. Newer preparations which have halogens in the ortho position can be used for comparison. It cannot be said with certainty what causes the improvement in effect through the inactive nuclear halogens. Perhaps the halogens participate in the reactions with the surfaces under the extreme conditions at which they help to further improvement. Fluorine Chlorine and Bromine have shown themselves in these experiments to be of equal value. First it was thought that the acidity plays a decisive role and that the halogen helps the diphenylphosphate to reach our optimum value. Chlorophenol is known to be more acid than phenol. Exact pH measurements did not support this assumption. The results of the measurements are reported briefly. They were carried out with a quinhydrone electrode.

<u>Substance</u>	<u>Concentr.</u>	<u>pH Value Measured By Quinhydrone Electrode</u>	<u>pH Value Measured with a Folien Colorimeter</u>
Diphenyl phosphate	10^{-4} Mol/l	2.0	2
Di-p-chloro phenyl phosphate	10^{-4} Mol/l	1.9	2
Di-p-nitrophenyl phosphate	10^{-4} Mol/l	2.0	2
Diphenyl phosphate	0.1 Wt.%	2.7	2.7
Di-p-chlorophenyl phosphate	0.1 Wt.%	2.4	2.5
Di-p nitrophenyl phosphate	0.1 Wt.%	2.4	2.5

One criterion for the opinion that the halogen acts only under extreme conditions would be the behavior of phenylphosphinic acid dipara-chlorophenyl esters. The halogen-free ester does not reach such extremely high values (over 900 kg/square centimeter) and therefore the halogenized ester does not bring much improvement.

Since the determination of the acidity did not bring any progress, other experiments were undertaken in order to clarify the processes that go on on the metal surface. I want to observe beforehand that a friction value of 0.01-0.1 as we have it normally on the Siebel-Kehl machine would be considered now in the region of partial lubrication (mixed friction).

Although this lubrication condition probably prevails in many technical bearings (running in) it is avoided by most authors that dealt recently with oil testing. They direct their attention primarily to boundary lubrication since lubrication capacity could not be evaluated on machines on which partial lubrication prevailed. Boundary lubrication is more comprehensible and there are many possibilities for explaining the effect of certain additives. But it is certain that lubrication capacity evaluations as they are determined by the Siebel-Kehl machine can be transferred qualitatively to technical bearings (see part 4) and this is decisive in these experiments. We also made experiments with our preparations on the four ball apparatus of Boerlage. These also were proven practical, particularly if surface treated balls were used. The friction circumstances of the four ball machine correspond closely to the boundary friction conditions in particular when surface treated balls were used. The sequence of effectiveness does not coincide exactly with that of the Siebel-Kehl machine. Experiments on boundary lubrication equipment with miniature friction surfaces did not lead to any results. Since alloying of the P with the metal surface (see Boeck 149 and FP861957 159) need not to be considered at the mild experimental conditions that prevail first but the friction value is decreased immediately, there remains the possibility of adsorption and

that of reaction of the additive. We have tried to reduce the concentration of the additives which were dissolved in benzol, by shaking them with iron powder. At an experimental temperature of 20°C we could not obtain informative results in this manner. Also the comparison of velocities of oil drops on a glass plane as advised by Collingrig (155) was in vain. After that we undertook to determine the accumulation of active materials in the liquid surface through measuring the surface tension. This was also in vain. As Professor Glockner reports, no reproducible results were obtained in adsorption tests with the aid of metal disks. After centrifuging off parts of the oil the weights of these disks were determined and compared. Finally we used method that was developed by Shell N. V. de Petrol Maatschap. Five g. of pulverized iron is mixed with 5 g. of oil and 3 cubic centimeters benzol. Then put 200 cubic centimeters of 10% sulfuric acid on a glass filter that is set over a suction flask. A stream of carbon dioxide flows through the flasks so that no sulfuric acid drips through the filter. The iron mixture is added to the sulfuric acid and allowed to react for 10 minutes. Then the CO₂ flow is shut off and the liquid is sucked into the flask. One determines the dissolved iron through titration with N/10 KMnO₄ and thus one obtains a criterion for the wetting power. If "a" denotes the amount of iron going into solution in the blank test, "b" denotes the dissolved amount of iron in the 10 cc filtrate in the oil test, "g" denotes the grams of oil added and "z" denotes the wetting power; then

$$z = \frac{(a-20b)100}{a \cdot g}$$

We obtained the following z values in our measurements.

"ROTRING" pure	2.0 ± 0.2
"Rotring" + 1% Triphenylphosphate	7.6
"Rotring" + 1.2% Phenylphosphoric acid diphenyl ester	8.2
"Rotring" + 1.0 Phenylphosphinous acid diphenyl ester	13.6
"Rotring" + 1% Diparacchlorophenyl phosphate	26.1
Rotring + 1% 891 I.G.	29.0

It was shown also that the very effective Diparachlorophenyl phosphate which has a low friction value in the first place clings well to the surface. The comparatively low wetting power of phenyl phosphinic acid diphenyl ester shows that its adsorption is not the decisive factor in its influence on lubrication. Based on the above results we conclude (as mentioned before) that adsorption on the metal surface occurs comparatively quickly with effective substances. The arrangement of such "epi layer lamination" has been observed by means of X-rays and electrons. With increasing load the reaction on the surface becomes more important. The unevennesses (flaws) are removed first since they are the spots with the highest load and therefore greatest heat, highest rate of reaction, and greatest thickness of additive, reaction products and lubricating oil molecules form a very stable film on the highly polished surface. We could especially well observe with the bare eye the formation of the surface film by the very aggressive phosphorylchloride. The formation of definite compounds was not yet proven. It was to be predicted from extensive experiences in the phosphating of metals that reaction products containing P would influence the friction favorably. In part 4 there are figures that show that the location of the corrosion point and welding point is improved by the use of bonderized balls in the four ball apparatus. (See Figure 50).

In the following we shall compare the substances used by us according to their composition and effect. For that purpose there follows a summary of their composition formula. "4" indicates good increase in carrying capacity, "0" a medium increase and "-" no increase. The friction values behave usually alike for the additives chosen by us. (This is not true for i.e. sulfur). Exact results are summarized in part 4.

It is striking that completely symmetrically built substances like 28 and 33 have no influence on lubricating properties, although they contain tri-valent phosphorus. Also 30, which contains an aryl group and two alkyl groups acts like them. Apparently they lack the ability to come into close contact with the surface and to accumulate on it. When a thin lubricating film was formed at higher pressure, the small portion of additive was not enough to be effective. The neutral phosphoric acid esters 44, 48, 49, 50 and 16, 17, 18 act like that too. Neither the introduction of halogens into the nucleus nor the substitution of the O atoms by S have thereby caused an improvement.

Also the success that appeared at first through the exchange of an aryl group against an alkyl group (16, 17, 18) proved to be deceptive. Small impurities of monochloride caused a delusion of effectiveness. After the experiences with 30 the behavior of the neutral aryl alkyl phosphates is not surprising. On the other hand the effectiveness of the series 1, 4, 3, 5, 25, 26, 27 is surprising at first glance. 1 differs from 44 only in the absence of an oxygen atom and 27 differs from 44 through the lack of 2 oxygen atoms. And yet there is this completely different behavior in the lubrication. One must look for a clarification in the greater adsorption power of 1 and 27 and a greater reaction potential. Because the phenyl group borders directly on

the phosphorus atom, the molecule is able to cling to the metal or to react with it. The oxygen of the $P=O$ is only in the way in that reaction. This is shown in the lower friction coefficient that 27 has from the start as compared with 1. Generally this series shows a higher friction value than the phosphoric acid ester series. That can be traced to the lack of the OH group. The introduction of alkyl groups in the nucleus (25, 26) has not a great influence on the effectiveness but it facilitates the introduction of the oil since the solubility of the preparation increases greatly.

7 and 9 are very effective preparations. The improvement of 9 through halogens was already mentioned. These materials contain an acid OH group which apparently helps in the clinging to the metal.

The uneffectiveness of 45 shows that the phenyl group is necessary for connection with the oil. The introduction of halogens in place of the hydroxyl group (45, 14) raised the temperature resistance and lowered the effect slightly. If oxygen is replaced by sulfur (23, 24, 20, 21) the effect is reduced somewhat in each case. The combined sulfur is not active in these compounds and apparently does not even become effective at high pressure. Free sulfur in certain concentrations (0.008%) gives medium carrying capacity on the Siebel Kehr machine, but it has a high friction coefficient from the start. It only acts in the moment in which the metal surfaces begin to corrode and therefore it is not much suited as running-in lubricant.

The oxygen bridges between Phenyl and Phosphorus in 7 and 9 are not important for the effect since 38 (I.G. preparation 891) which does not have it is also very effective. It is rather stable to heat. It was preceded by 36 which is also very effective but it decomposes at $250^{\circ}C$. One can replace the OH groups in 36, 38 and 37 by halogens without changing the effect much. (2, 32) In 31 the chlorine atoms are replaced by hydrogen. This very effective preparation cannot be used because of other properties. It is worthy of note that also hydrogen atoms cause a clinging to the metal. It is true that a partial oxidation in the air of this particular preparation is not out of the question.

Let us mention, too, that the insertion of N between aryl and phosphorus groups destroyed the effect. (40, 41)

Looking at the construction of the particular compounds we can see the probability of the primary effect of the adsorption. It has not been ~~determined to date what kind of compounds are formed in the secondary effect,~~ the reaction with the surface.

Table 2

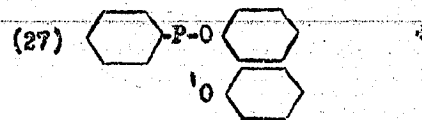
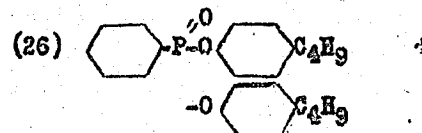
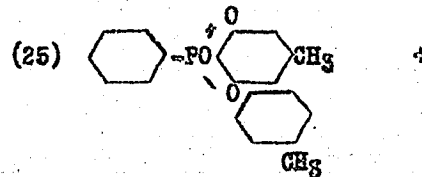
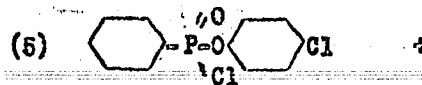
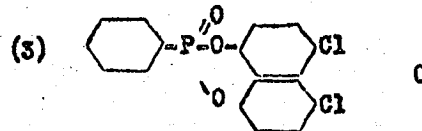
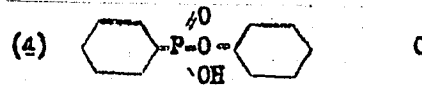
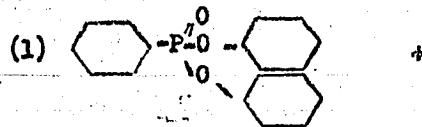
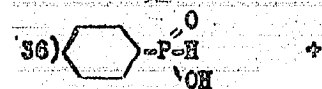
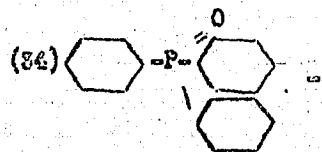
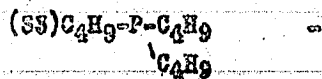
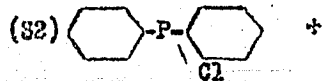
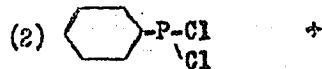
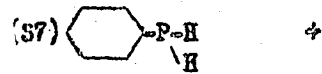
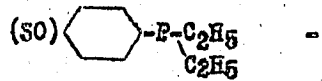
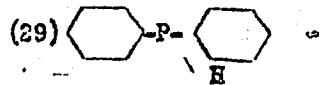
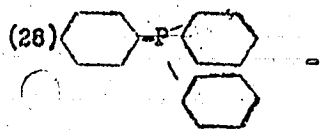


Table 2 (Cont'd.)

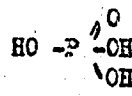
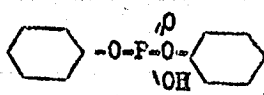
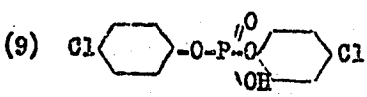
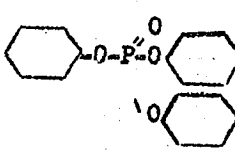
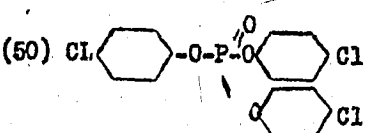
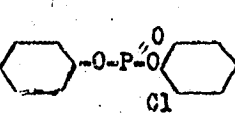
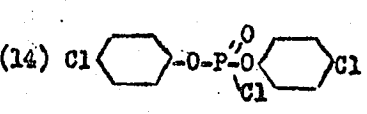
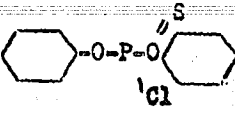
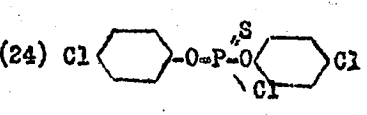
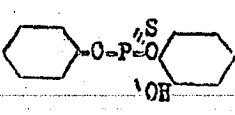
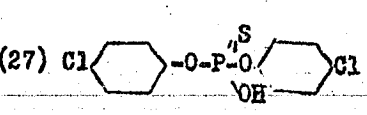
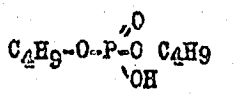
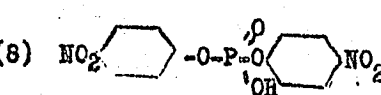
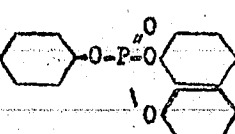
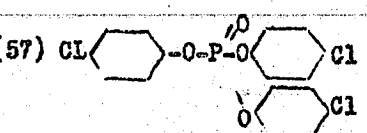
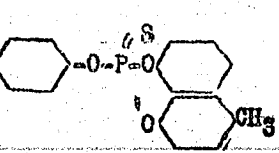
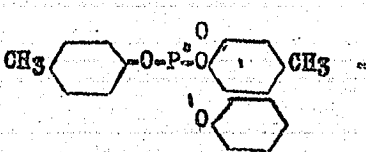
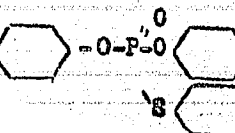
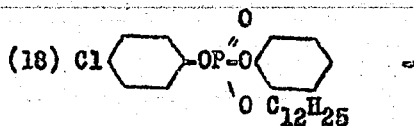
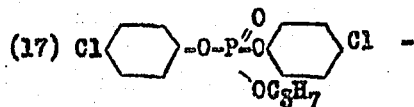
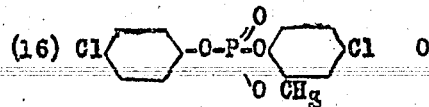
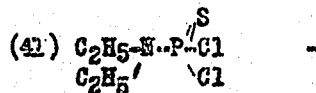
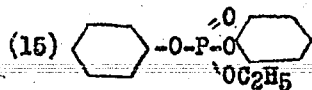
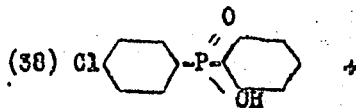
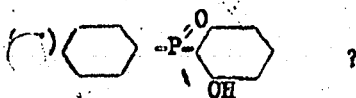
(43)		-			
(7)		+	(9)		+
(44)		-	(50)		+
(45)		+	(14)		+
(23)		0	(24)		0
(20)		+	(27)		+
()		0	(8)		0
(47)		-	(57)		-
(48)		-			
(49)		-			
(22)		-			

Table 2 (Cont'd.)



In the course of our investigation we have synthesized a fairly large number of phosphorus-containing compounds, part of which were unknown until now. The effect concerning the improvement of lubricants on test apparatus, bearing tests and also in motors has been proven for some of those. The use in the motor makes extraordinarily high demands on the preparations. Further tests also in gears are still in progress. One can consider for sure that the introduction of halogens in para position into the nucleus of aryl esters of phosphoric acid increases the effect while the introduction of alkyl esters increases the solubility in mineral oils.

II. Production of the Preparations

1. Phenylphosphinic acid diphenylester
2. Phosphenylchloride
3. Phenylphosphinic acid diparachlorophenylester
4. Phenylphosphinic acid monophenylester
5. Phenylphosphinic acid di-p-chlorophenylestermonochloride
6. Isopropylbenzoldichlorophosphine
7. Diphenylphosphate
8. Di-p-nitrophenylphosphate
9. Di-p-chlorophenylphosphate
10. Di-p-bromophenylphosphate
11. Di-p-fluorophenylphosphate
12. Di-2,4-dichlorophenylphosphate
13. Diacetylphosphate
14. Di-p-chlorophenylphosphoric acid monochloride
15. Diphenylphosphoric acid ethylester
16. Di-p-chlorophenylphosphoric acid methylester
17. Di-p-chlorophenylphosphoric acid propylester
18. Di-p-chlorophenylphosphoric acid lauryl ester
19. Phosphorsulfochloride
20. Diphenylthiophosphate
21. Di-p-chlorophenylthiophosphate
22. Diphenylphosphoric acid thiophenylester
23. Diphenylthiophosphoric acid monochloride
24. Di-p-chlorophenylthiophosphoric acid monochloride
25. Phenylphosphinic acid diacylester
26. Phenylphosphinic acid di-p-butylphenylester
27. Phenylphosphinous acid diphenylester

Substances Prepared for the First Time

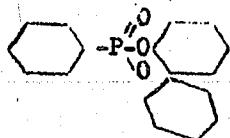
No.	Name	melting point (K)	
3	Phenylphosphinic acid di-p-chlorophenylester	boiling pt. 13	67.5°-69.5° (pure) 276°-277°C
5	Phenylphosphinic acid mono-p-chlorophenylester monochloride	boiling pt. 760	320°-435°C not isolated
10	p-bromophenylphosphoric acid chloride	boiling pt. 20	155-170°C not purified
10	Di-p-bromophenylphosphoric acid monochloride	boiling pt. 20	260°-280° not purified
11	p-fluorophenylphosphoric acid dichloride	boiling pt. 15	134°-145° not purified
11	di-para-fluorophenylphosphoric acid monochloride	boiling pt. 15 84	180°-210° not purified 210°-213° pure
11	Tri-p-fluorophenylphosphate	boiling pt. 16	235°-250° not purified
11	Di-p-fluorophenylphosphate	melting pt. (K)	95°-96° pure
12	Di-2,4-dichlorophenylphosphate	-	not purified
16	Di-p-chlorophenylphosphoric acid methyl- ester	melting pt. (K)	131°-132° pure
17	Di-p-chlorophenylphosphoric acid propyl- ester	melting pt. (K)	113.5-114.5 pure
18	Di-p-chlorophenylphosphoric acid lauryl- ester	melting pt.	90°-100°
21	Di-p-chlorophenylthiophosphate	-	-
22	Diphenylphosphoric acid thiophenylester	boiling pt. 28	288, 290°
25	Phenylphosphinic acid diocresylester	boiling pt. 26	255-276° not purified
26	Phenylphosphinic acid di-p-butyl phenyl- ester	boiling pt. 20	305-316° " "
27	Phenylphosphinous acid diphenylester	boiling pt. 15	225-228 pure

Newly Determined Constants for Known Substances

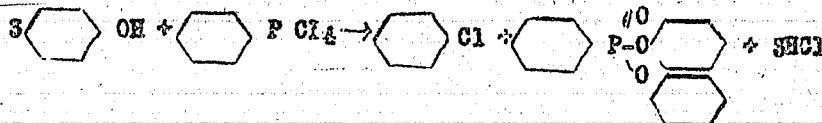
Phenylphosphinic acid diphenylester	m.p. (K) 73-74°C	Michaelis	1.2 m.p. 63.5°
Di-p-chlorophenylphosphate	m.p. (K) 130-131°C	Anthenrieth	20 37 m.p. 126°-127°
Triparabromophenylphosphate	b.p. 20 320°-555°	Zedzscho	m.p. 133°-135°
Di-p-bromophenylphosphate	m.p. (K) 63.5°	Zetzsche	87 m.p. 199-201°
Di-p-chlorophenylphosphoric acid monochloride	m.p. (K) 53°-54° b.p. 225-226°		
Tri-p-chlorophenylphosphate	m.p. (K) 112-113° b.p. 18 292°-295°	Anthenrieth Agfa	20 21 m.p. 99-100° m.p. 112°

1. Phenylphosphinic acid diphenylester

(Beilstein) 16/804



Michaelis and Hammerer 1,2 have prepared this ester first. They obtained a thick oily liquid that boiled above 360°C and solidified upon cooling the substance was easily soluble in benzol, ether, and ethanol. One could obtain white needles with m.p. 63.5° from aqueous alcohol. Aqueous caustic soda had no effect on the ester, alcoholic caustic soda decomposed it into phenol and phosphophenyl acid. The synthesis occurred according to the following equation:



We started also with Phosphorylchloride in the preparation. We conducted a strong current of dry chlorine into 500 g. of it under ice water cooling until the whole mass solidified into tetrachloride. That took 2-3 hours. After addition of 1 kg. of phenol the liquid mass was stirred vigorously for a while until the formation of HCl (which escaped in torrents) subdued. Then it was distilled by means of a salt bath. In the beginning the thermometer rose

steadily and a mixture of phenol and chlorobenzol was distilled off. At continued distillation under normal pressure the ester passed over at 370°-380°C and was slightly yellow. Later batches were distilled in a vacuum and the ester that came over at b.p. 20-260-270°C was entirely colorless. The yield fluctuated between 95-100% (calculated on the phosphorylchloride). The solidified product began to melt at 64.5°C (K). The melted mass only became clear at 69-73°C depending on the starting batch. After repeated recrystallization from ethanol the melting point was 73-74° (K).

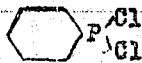
16.7 mg subat. (dried in vacuum): 42.5 mg CO₂, 7.4 mg H₂O
C₁₈H₁₅O₃P (310) calculated C 69.7 H 4.8
found C 69.4 H 5.0

During production of larger amounts the distillation of the ester was not carried out, since also the light brown colored crude product sufficed for our purposes.

In order to test the decomposition of the ester by boiling water, we boiled 20 g. for 2 hours in an excess of water. The starting material was recovered unchanged after processing. The production of larger amounts of the ester were used for testing its reactions. Starting with 500 g. Phosphorylchloride and 1000 g. of phenol we caught the ester resulting from the distillation up to 181.5°C. It amounted to 374 g. During rectification it boiled between 137°-181.5°C. Through experiments (distillation of mixed chlorobenzol and phenol) it was determined that the two components from mixtures that boil together, and that cannot be separated through fractionation. Therefore the phenol content was determined by volumetric analysis. It amounted to 19.78%. The remainder of 246 g. had to be Chlorobenzol. Through treatment with the calculated amount of NaOH in a little water, the phenol was removed. The remaining liquid boiled constant at 133°. The yield of chlorobenzol amounted thus to 77.1%. A large part of the missing 21.9% (sic:translator) probably escaped during the vigorous formation of HCl.

2. Phosphorylchloride

Beilstein 16/763 (421)



Earlier I prepared 4 kg. phosphorylchloride according to Michaelis' second method (4, 5, 6) that had been improved by Grütter and Wiernick (7). ~~Melzer-heimer (8) who has worked with both methods considers the aluminum chloride method much more convenient.~~ In my opinion it has a number of decisive disadvantages as compared with the pyrogenic method of production. These disadvantages hinder the production of large amounts. Particularly now it is

difficult to procure large amounts of sufficiently pure aluminum chloride. Commercial $AlCl_3$ reduced the yield considerably. The entire aluminum chloride as well as large amounts of benzol and PCl_3 are lost in the process. The undesirable aluminum chloride grease requires extensive cleaning work. Also a vacuum distillation is necessary each time which is not an enjoyable task when carried out in vessels over 4 l. in the laboratory. Finally it was shown that larger amounts of starting materials (1 kg. benzol and 1 kg. PCl_3) gave considerably smaller yields than the starting amounts that I chose usually (400 g. of each). This is contrary to the usual experiences. No yield improvement was brought about by the use of aluminum chloride manufactured by us, of aluminum and sublimate or through additions of calcium carbonate, boric acid, phosphorpentoxide, stannic tetrachloride and silicon tetrachloride.

Then the firm that was given the task of working out a method of production turned to the method that was indicated by Bowles and James (10). There the heating of the quartz apparatus (built according to their directions) gave difficulties. Wire of chrome-nickel of various thickness and even tungsten wire proved to be insufficient. Experiments with silicon carbide sticks and chrome-nickel band gave no positive results so far. This method did not seem suited for production on large scale because of apparatus difficulties. Yields of 80 g. in 24 hours were the maximum reached so far.

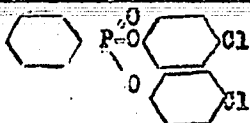
Therefore I decided to carry out Michaelis' first method in improved apparatus. It consists of a reaction of benzol and phosphorotrichloride when heated. Michaelis obtained on an average only 100 g. in 10 hours, Pope and Gibson (12) raised the yield to 140 g. in 9 hours by introduction of CO_2 . Arbuzow (13) reached 1-1/2 times the yield of Michaelis by filling the heating pipe with unglazed pieces of clay and Meisenheimer writes of a further increase through the use of a quartz pipe. I could show that one can easily obtain 5-6 times the yield of Michaelis. That way one can produce 1 kg. phosphorochloride in one apparatus in 24 hours.

Important points in my apparatus were as follows. The pipes were all chosen wide in order to prevent clogging up as much as possible (for measurements see Figs. 1 and 2). The connections were made of rubber, and in places that were in contact with hot fumes they were made of water glass-talcum-asbestos. This cement (lute) was very good. Continuous operation was made possible by installing a branch pipe on the reflux pipe for refilling. The CO_2 current was set for 3 bubbles per second. This fast current was to push the vapors relatively quickly through the red hot pipe. The heating was done by gas which produced a medium red heat. A temperature reading on an optical pyrometer on the outer pipe wall gave 800-850°C, a temperature reading during the reaction in the interior of the pipe gave 750-750°C. The first runnings that resulted in the distillation of the reaction products were reused always at least partially in the next batches.

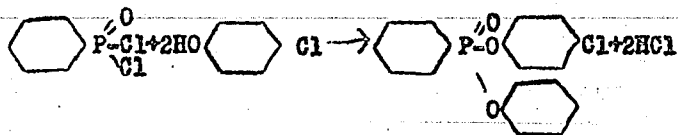
<u>PCl₅</u> <u>cc</u>	<u>C₆H₆</u> <u>cc</u>	<u>First Run Distil.</u> <u>cc</u>	<u>Running Time</u> <u>Hrs.</u>	<u>Yield C₆H₅PCl₂</u> <u>g</u>
500	500	-	6	190
750	750	-	18	350
250	250	1000	25	800
500	500	500	16	850
700	700	100	12	575
600	600	500	14	800
600	600	100	14	900

Experiments with steel pipe gave also usable results.

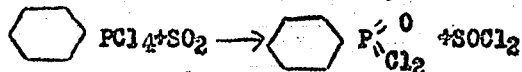
3. Phenylphosphinic acid-di-p-chlorophenylester



This compound was not described in the literature until now. It was prepared like the chlorine-free substance from which it is derived (1, 2).



The dichloride can be produced from Phosphenylchloride and oxygen (3,14) or it be made from the tetrachloride with SO₂ (1,14). We chose the later method and obtained the dichloride as thick liquid b.p. 257°-265°C (uncorrected) with a yield of 92% calculated on phosphenylchloride.



In the preparation of the ester we used a solvent. 40 g. chlorophenol, 50.5 g. dichloride and 50 cc benzol were heated on a water bath till no HCl could be detected in the gas stream. During the heating, under a superimposed reflux cooler, N₂ was conducted through. The HCl vapors stopped after 12 hours. The benzol was steamed off and the residus was distilled in vacuum. The boiling point was b.p. 13 276°-277°C. The yield was 43 g. That is about 74% of the theoretical yield. The thick oil at first does not even crystallize in the ice box at -14°C, but after several days it solidifies spontaneously. In order to remove possible residual chloride, we treated it with hot water, shook it with ammonia and recrystallized it using aqueous alcohol. Melting point was (K) 67.5-69.5.

Chlorination of Phenylphosphinic Acid Diphenylester

It was attempted to chlorinate the ester directly and thereby to introduce 3 Cl atoms. For that purpose 100 g. of the ester was treated with chlorine, mixing in some iodine and using a temperature of 90°-100°C. A chlorine absorption of about 8.5 g. per hour resulted. After 4 hours the weight had increased by 34.5 g. which could correspond to the desired chlorine absorption.

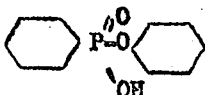
The product of reaction was fractionated in a 13 mm vacuum. The 132 g. of crude product gave a first fraction (10 g.) of fat-like consistency and yellow color. Then came a main fraction at a boiling point b.p. 13, 255°-300°C in the form of a highly viscous yellow liquid (85 g.). The residue was a black asphalt-like mass (25 g.).

The chlorine determination showed that only 2 atoms of chlorine had entered. They were probably in the phenol nuclei (rings) 30.85 mg. of the substance gave 25.44 mg. AgCl (Carius)

found Cl = 18.80%, calculated for 2 Cl atoms 19.78%

4. Phenylphosphinic acid monophenylester (3,14)

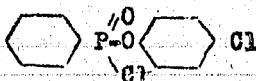
Beilstein 16/804



As in preparation 3, phenylphosphinic acid dichloride was produced first. 27 g. dichloride and 13 g. phenol were heated under reflux under a N_2 stream until no more HCl was formed. Then it was fractionated. First came a small first fraction, the main fraction came at 320°-380°. The distillate was boiled with water in order to saponify (hydrolyze?) the chloride. The residue which solidified upon cooling was treated with concentrated aqueous ammonia at 50°C. The remaining diphenyl ester (9 g.) was filtered off and the monophenylester was precipitated with hydrochloric acid. For complete separation we allowed it to stand overnight.

In an attempt to avoid the formation of diphenyl ester we started out with sodium phenolate and treated it with the dichloride as above. But here, too, a large amount of the neutral ester was obtained.

5. Phenylphosphinic acid mono-p-chlorophenylester-monochloride



We have seen to it that the formation of the neutral ester is largely suppressed since it cannot be separated through distillation nor in this case with ammonia treatment. That was accomplished by completing the reaction in as short a time as possible. 20 g. phenylphosphinic acid dichloride and 14 g. chlorophenol were

heated for 2 hours under reflux and were immediately distilled. After a prefraction at 300°-320° (1 g.), a main fraction of 320-435° (18 g.) was caught. A small after-fraction came at 435-440°C. A small amount of black residue remained.

In order to determine the monochloride we heated a small amount of the distillate with N/10 NaOH to boiling for 1/4 hour and back-titrated the excess alkali. On a sample of 1.7567 g. of distillate 104.15 cc of N/10 NaOH was used. According to that the content of monochloride amounts to 87.8% of the main fraction. That is a 56.69% yield calculated on the starting materials. In calculating the used amount of sodium hydroxide one must take into account that 1 mol. of chloride will use 2 mols. of NaOH. In the blank test neutral ester was heated with NaOH. No N/10 NaOH was used there.

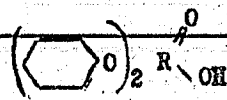
6. Isopropylbenzoldichlorophosphine (15).



To 250 g. of Isopropylbenzol and 10 g. of water-free aluminum chloride, 290 g. Phospho trichloride were added drop by drop with stirring. Then it was heated for 48 hours over a sand bath under reflux. During that time additional 15 g. of aluminum-chloride was added in 2 portions, when the HCl formation had become weak. The stirring was continued only during the day (20 hrs. altogether). After conclusion of the reaction the unchanged phosphortrichloride was distilled off under normal pressure. Then the isopropylbenzol was distilled off under reduced pressure. The residue consisted of a red liquid and a light crust. The liquid was poured off the solid constituents and fractionated at 10 mm. The prefraction was small, then 75 g. of colorless liquid was gained at b.p. 125°-127°C. The yield was 16% of the theoretical one calculated on isopropylbenzol. The isopropylbenzoldichlorophosphine was fractionated once more in a vacuum. The thickly liquid residue contained also considerable amounts of the phosphine. In order to avoid a loss it is practical not to process it further but it serves as a catalyst in the next run in place of the aluminum chloride.

7. Diphenyl Phosphate

Boilstein 6/178 (95)



The phosphoric acid esters of aliphatic and aromatic oxygen bodies have constantly gained in importance in the last 20 years. The neutral phenol esters of various phenols are used to a large extent as softeners, insulators, wetting agents, lubricants and for purification of waste-gases and waste-waters. In addition

to that there are a number of smaller spheres of use. Since I started with neutral esters in my preparation of di-substituted esters, I would like to give a short survey about their manufacture. Triphenylphosphate was prepared, first by Jacobsen (16) and then by Heim (17), out of phenol and phosphoricoxychloride by heating and following fractionation. Phenylphosphoric-acid dichloride (b.p. 121° (18) and diphenylphosphoric acid-monochloride (b.p. 195° (18) are formed as by-products. The neutral phenol ester melts at 49° (19) and has a b.p. of 245°. Athenrieth prepares it by reacting an alkaline phenol solution with phosphoricoxychloride in the cold (20). Agfa prevented the formation of larger amounts of by-products and the annoying appearance of HCl by reacting POCl₃ with sodium phenolate (21). A facilitation of Jacobsen's reaction was reached by the Imperial Chemical Industries Ltd. (22,23) by the addition of basic compounds like aniline, pyridine, toluidine (see also Fischer (24)). Adicks, Brunert, and Laskaer (25) and the Dow Chemical Co. (26) used SnCl₄, AlCl₃ and MgCl₂ successfully as catalysts. In the case of the Celluloid Corp. (27) PCl₅+H₂O serve as a substitute for phosphoricoxychloride. The Victor Chemical Works (28) use pentachloride and pentoxide. Methods of lesser importance are the reaction of diarylsulfite with PCl₅ by Carré and Libermann (29) and the oxidation of triphenylphosphite by means of air, SO₃, nitrogenoxides and the appropriate catalysts like vanadium pentoxide (30,31).

Of all the above processes, only the reaction of alkaline phenol solution with POCl₃ according to Athenrieth (20) yields diphenylphosphate immediately. Rembold (32) described the formation of this ester out of P₂O₅ and phenol. Glutz (33) described the preparation through hydrolysis of triphenylphosphate with a strong alkali. Jacobsen (16), Rapp (34), Hoeftake (19), as well as Brigl and Miller (35) hydrolyzed the monochloride with water or dilute alkali.

Since we had commercial triphenylphosphate available, we first started with it. We treated 1 mol. neutral phosphate suspended in water with 2 mols. H₂OH. A very violent reaction occurs at heating to boiling of the water when larger quantities are used. The clear solution is acidified with HCl. Thereby the typical phenol odor appears. Then it is mixed with an excess of sodium carbonate and the phenol, that was not converted into the sodium salt, removed by six extractions with ether. In the beginning a fairly large quantity of ether dissolves in the liquid. The ether is removed on a water bath and allowed to cool. Upon acidification the diphenylphosphate precipitates as fine white crystals. It is filtered with suction and dried in the air. The yield is quantitative. Experiments to remove phenol with ~~steam were not very successful. The largest starting quantity that was processed at one time by us in this manner was 2 kg. triphenylphosphate.~~

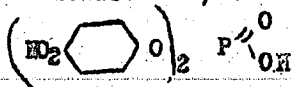
In the trial preparation according to Athenrieth (20), 94 g. phenol and 52 g. POCl₃ resulted in 87 g. triphenyl- and 14 g. diphenyl-phosphate.

Another experiment dealt with the hydrolysis of the monochloride. 306 g. POCl₃ and 376 g. phenol resulted after 20 hours of heating in 50 g. dichloride and 255 g. monochloride. The latter readily gave diphenylphosphoric acid upon heating with dilute alkali.

The ester precipitated by HCl is not a uniform product. The melting points of the substances obtained thus are very different and there are also large differences in the solubility. Thus we determined in the air-dried substances melting points of 66-68°C, 67°-69°C, 48-100°C, 49°-115°C. Under certain experimental conditions there results a water-free substance directly (m.p. 70°C, Hoefheke (19)) while in other cases a mixed preparation is present. But all these products change upon exposure to air for several days either into the diphenylphosphate containing 2 H₂O m.p. (K) 50°-51° or into the water-free product m.p. (K) 68-69.5°. One always obtains the water containing preparation in beautiful crystals when it is recrystallized from boiling water. Thereby a portion always remains in the solution, which must be reprecipitated with acid. The water-free diphenylphosphate forms always when it lies in the vacuum dessicator. We did not study in detail the intermediate product with the higher melting point, which caused the large melting point intervals and gave the abnormally low oil solubility to the entire product. It may be a pyrophosphate. One can explain also the contradicting information in the literature by all these conditions. Rapp (34) gives the melting point as 56°C, Anthenrieth (20) at 61°-62°, Hoefhake (19) has correct values at 51° and 70°. In order to try whether diphenylphosphate can be distilled, the substance was slowly heated in an oil bath at 0.09 mm. Hg. At 210°-230° in the oil bath, crystals began to deposit in the receiver. But they melted much below 45°. Thus the ester had already decomposed and the phenol was distilled off.

8. Di-p-nitrophenylphosphate

Beilstein 6/237



In the preparation I tried first to start out with triphenylphosphate, to nitrify it and then hydrolyse it, but the molecule split completely in the hydrolysis. 25 g. finely pulverized triphenylphosphate was stirred into 100 g. 100% HNO₃ at -3° to -5°C. Then the stirring continued for 3 hours at 20°C. The nitrated product is precipitated out of the homogeneous liquid with water. It is filtered under suction and washed free of acid with water. The yield was 35 g., that is, 95% of the theoretical yield. The product was recrystallized from glacial acetic acid, its melting point was then m.p. (K) 156-157°C. Rapp (34) gives 155° as m.p. 5 g. of triphosphate were heated in a water bath with 0.5 g. NaOH in alcoholic solution for one hour. Then it was processed as usual. Thereby we could only isolate p-nitrophenol. Since

triphenylphosphate was hydrolyzed successfully in this manner, the failure in hydrolysis must be caused by the nature of the tri-p-nitrophenylphosphate. An earlier trial to nitrify the triphenylphosphate with 65% nitric acid resulted only in unchanged starting material. Another test dealt with the usual method of heating phenol with phosphoricoxychloride. First HCl developed as usual. Upon higher heating charring with swelling took place suddenly. We noticed later that Rapp (34) had found that also. Perhaps this reaction can be carried out by keeping the temperature down constantly.

Neither did shaking of p-nitrophenol in alkaline solution with phosphorus oxychloride lead to a result (according to Authenrieth (20)).

Only p-nitrophenol was obtained from nitrifying diphenylphosphate with 100% HNO₃. The process of Rapp (34) gives only very small yields.

Finally the preparation was obtained with good yield according to Hoeflake (19). 10 g. diphenylphosphate is added to 30 cc HNO₃ with stirring at -5° to -10° and the resulting liquid is poured into water immediately. Thereby an oil is separated which solidifies in the ice box overnight. It is washed with concentrated HCl. In order to free the product of isomers it was recrystallized twice in glacial acetic acid. The m.p. was (K) 174.5°-175.5°. The crude product contains normally 15-16% O-nitrophenol.

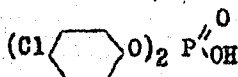
30.8 mg substance give 2.12 cc N₂ at 21°C and 750 mm Hg
22.30 " " " 1.65 " " " 26°C " 744 " "

found 7.8% N₂ calculated 8.2%
" 8.2% " " 8.2%

The preparation that was cooled in a vacuum desiccator absorbs 1 mol. H₂O in the air.

9. Di-p-chlorophenylphosphate

Beilstein 6/188 (-)



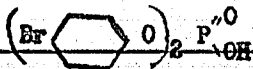
Also this ester is conveniently accessible in various ways. We produced it ~~once by hydrolyzing the monochloride, another time by reacting the triphosphate~~ with aqueous sodium hydroxide. By combining the two processes we could facilitate the production in large quantities in the laboratory. The triphosphate was prepared by Authenrieth from chlorophenol and phosphoric oxychloride in alkaline solution. A m.p. of 99-100°C was determined. Agfa prepared the ester from sodium phenolate and POCl₃ and reports a m.p. of 112°. Durrane(36) ~~obtained the product from triphenylphosphate and sulfurlychloride, using~~ pulverized iron as catalyst. The latter method requires a distillation of the

entire batch in order to remove the iron completely. Hence its use was out of the question. Also di-p-chlorophenylphosphate was obtained first by Authenrieth as a by-product in the production of triphosphate. He produced it also by hydrolysis of triphosphate with alcoholic caustic potash solution and obtained flakes of m.p. 126-127° out of diluted HCl. Zetzsche and Nachmann (57) found a m.p. of 133-135° (K) for their preparation which they obtained through hydrolysis of monochloride and neutral phosphate.

The starting material - p-chlorophenol - was obtained by the method of Dubois (38,39). Excess sulfurylchloride acted on phenol and isomers were separated by following fractional distillation. From two kg phenol and 3.2 kg sulfurylchloride that was added by drops in the course of 6 hours, we obtained 624 g. of 185-200°C and 1900 g. of 200°-217°C. The chlorophenol with the higher boiling point was purified by freezing and centrifuging. One mol. POCl_3 (153.5 g. + 30 g. excess because of loss, since HCl carries some of it away) is added dropwise to 3 mols. p-chlorophenol (385.5 g.) with stirring. It is heated till HCl development stops on the reflux. The reaction is completed in about 7 hours. Then the entire substance is boiled with aqueous caustic soda till it is water-soluble. Thereby triphosphate turns into diphosphate and dichloride into monophosphate. The latter decomposes into chlorophenol and phosphoric acid (40). Upon acidification di-p-chlorophenylphosphate contaminated with chlorophenol comes down as oil. It cannot be purified with soda since chlorophenol forms a salt with sodium too. Chlorophenol was removed to a large extent through steam distillation. This method did not seem suited for large quantities. The yield of crude diphosphate amounted to 255 g., that is, 70.5% of the theoretical yield (the entire reaction is calculated on triphosphate). During recrystallization in benzol, the excess phenol remained in solution. Finally it was recrystallized from water. Thereby the di-p-chlorophenylphosphate came out as shiny flaky crystals and had a m.p. of 130-131°C.

In the preparation of diphosphate from pure monochloride we added it dropwise to $2\text{NH}_4\text{OH}$ with stirring at 70-80°. After some time water had to be added once more to attain complete solution. We obtained 570 g. diphosphate out of 630 g. monochloride, that is, 95.5% of the theoretical yield. This method is convenient since it spares tedious cleaning operations.

10. Di-p-bromophenylphosphate



Until now tri-p-bromophenylphosphate prepared by Authenrieth and Müllinghaus had been obtained of the p-bromophenylphosphoric acid esters. They reacted phenylacetate with PBr_5 and got the ester in small quantities with a m.p. of 101°. Glutz (35) obtained the same compound from triphenylphosphate and bromine in a sealed tube. Zetzsche and Nachmann got the di-p-bromophenylphosphate from

diphenylphosphate and bromine in boiling chloroform and found the m.p. of 199-201 for the substance after recrystallizing in water or CHCl_3 . Also the less interesting monophosphate is known (37,42).

Since we needed larger quantities of the material we turned to more productive methods of production. We reacted brown phenol with phosphorexychloride. The necessary p-bromophenol was prepared according to the method of Marvel and Adams (43). One reacts bromine with phenol in carbon disulfide with stirring and cooling. Then fractionate the mixtures of isomers after removal of the solvent by means of a column. We used for that purpose a layer of Raschig rings 3 cm high. The boiling point of the obtained p-bromophenol was Kp_{25} 146-150°C. The yield was 750 g. for a starting amount of 500 g. phenol, that is, 81% of the theoretical yield.

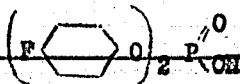
340 g. p-bromophenol (1 mol.) were heated to 190°C and 1 mol. phosphoroxychloride was stirred in drop by drop. Vigorous HCl was developed. After completing the addition it was heated on the reflux for 10 hours and the reaction product was fractionated.

120 g. p-bromophenylphosphoric acid dichloride b.p. 20 155-170
200 g. Di-p-bromophenylphosphoric acid monochloride b.p. 20 260-280
105 g. tri-p-bromophenylphosphate b.p. 20 320-335°

The various fractions were not purified further. To produce the diphosphate one can hydrolyze the monochloride or the trichloride bromophenol is split off when triphosphate is boiled with aqueous caustic soda. Diphosphate goes into solution as sodium salt and can be separated again with conc. HCl as light-colored oil. Upon washing with cold water the oil solidifies to a colorless crystalline substance. This is recrystallized from hot water. The diphosphate crystallized to shiny flaky crystals and has a melting point of (K) 162-163.5°C.

Diphosphate could also be prepared of di-p-bromophenylphosphoric acid monochloride, which solidifies at room temperature, by boiling it with aqueous sodium hydroxide. The melting point was 163.5°. Curiously Zetzsch and Nachmann found a much higher melting point 199-201° (37).

11. Di-p-fluorphenylphosphate



Phosphoric acid esters of p-fluorophenol are not known up to date. p-fluorophenol was obtained in the boronfluoride process of Schiemann (44) using anisidine. Freshly distilled anisidine was diazotized and the diazonium solution was reacted with fluoboric acid with cooling. The resulting paste was filtered and

the solid portion was dried in a vacuum desiccator. Then the pyrogenic decomposition occurred. The resulting fluoranisol was hydrolyzed by means of aluminum chloride. A good yield of fluorophenol of b.p. 61° - 84° was obtained.

26 g. p-fluorophenol (2 mol.) were heated with 19.4 g. POCl_3 (1 mol.) for 15 hours on the reflux till no HCl was formed. The reaction product was fractionated.

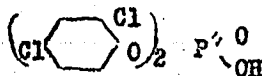
p-fluorophenylphosphoric acid dichloride b.p. 134 - 145°

di-p-fluorophenylphosphoric acid monochloride b.p. 15 180 - 210°

tri-p-fluorophenylphosphate b.p. 235 - 250°

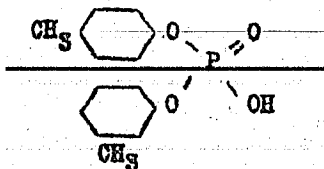
The yield of crude monochloride was 18 g. It was redistilled and had a b.p. of 210 - 213° . After reacting it with aqueous soda lye and spreading it out as usual the diphosphate was obtained. Contrary to the chlorine and bromine derivatives, the fluorine derivative only leaves the water upon acidification. We obtained five shiny flaky crystals which showed a m.p. (K) 95° - 96°C after drying it in vacuum. During the C determination the substance proved to be difficultly combustible and gave values that were too low. The triphosphate solidifies likewise in the cold.

12. Di-2,4 dichlorophenylphosphate



The 2,4 dichlorophenol was prepared according to directions of Kohn and Sussmann (45) by introducing diluted chlorine into phenol while cooling. The resulting product was free of isomers. Then it was reacted with the corresponding quantity of POCl_3 . Without fractionating it was then hydrolyzed with caustic soda. The diphosphate was isolated as usual. First a light colored sirup was formed which crystallized in the ice box after a few days.

13. Diacetylphosphate



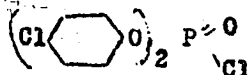
Diacetylphosphate was obtained as reddish sirup by heating commercial triacetylphosphate with NaOH .

Experiment with Dichlororesorcinol

Dichlororesorcinol was prepared according to Reinhard (46) and was heated in the reflux with POCl_3 . A resinous brittle compound was formed which could not be hydrolyzed with NaOH .

14. Di-p-chlorophenylphosphoric acid monochloride

Beilstein 6/188



This chloride was obtained by Athenrieth (20) by heating di-p-chlorophenylphosphate and PCl_5 . It was not isolated from the solidified substance but was immediately reacted to the amide. We produced the preparation by reacting chlorophenol with phosphorochloride. 1280 g. crude p-chlorophenol (b.p. 202-218) were heated with 875 g. POCl_3 for 19 hours. The product was fractionally distilled:

430 g. p-chlorophenylphosphoric acid dichloride b.p.₂₆ 160-220°

1050 g. di-p-chlorophenylphosphoric acid monochloride b.p.₂₅ 220-270°

260 g. tri-p-chlorophenylphosphate in the residue

327 more monochloride and fairly large quantity of triphosphate was obtained upon heating the 430 g. dichloride with 260 g. p-chlorophenol. The pre-fraction was only 35 g.

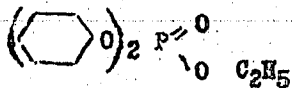
The monochloride had a b.p.₁₅ of 225-226° after repeated fractionation. Analysis according to Carius: 200.7 mg. substance 257.0 mg $\text{AgClC}_{12}\text{H}_9\text{O}_3\text{Cl}_3\text{P}$ (357.5) found: Cl 31.7% calculated 31.3%.

Even after standing several days at -15°C , the oily colorless liquid did not solidify at first. After about 3 weeks spontaneous crystallization occurred. Out of hexane we obtained colorless, nearly odorless crystals of m.p. (K) 53-54°C.

The triphosphate was also distilled b.p.₁₈ (292-295) and recrystallized after dissolving it in ether. The melting point was (K) 112-113°C.

15. Diphenylphosphoric acid ethyl ester

Beilstein 6/179



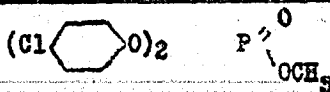
The following methods are possible for the preparation of such mixed esters:

1. Reaction of triphenylphosphate with sodium alcoholate (Morel(217)).
2. Reaction of diphenylphosphoric acid monochloride and sodium alcoholate (Morel (48)).
3. Use of phosphoric acid alkylesterdichloride and sodium phenolate (Morel (47)).
4. Direct esterification of diphenylphosphoric acid with alcohol with corresponding removal of water perhaps through CaC_2 in the apparatus of Thielepape.
5. Starting with monochloride and alcohol with addition of a substance that splits off HCl like pyridine.
6. Reaction of (diphenylphosphoric acid sodium) with an alkylhalogenide.

Methods 1 and 4 did not yield much in preliminary experiments, no reaction was obtained in method 6. Therefore we proceeded according to method 2. The monochloride was prepared (according to Rapp (34)) by heating 188 g. phenol with 188 g. POCl_3 (1 mol. + 35 g. excess, see Ephraim (50)) for 14 hours under reflux. In the fractionization we obtained 125 g. monochloride of b.p. 25-215° and 80 g. dichloride.

The monochloride was reacted with the calculated amount of sodium alcoholate in ethanol. The reaction occurred with separation of NaCl. It was filtered, the alcohol vaporized off, and fractionated in vacuum. After a short prefraction the ester came. The boiling point 15 was 205-220°.

16. Di-p-chlorophenylphosphoric acid methyl ester

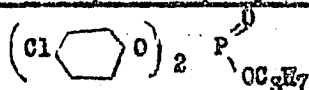


We started with monochloride also for the production of this compound which has not been known before. Salt was separated when we reacted it with sodium methylate. After filtration it was distilled in vacuum. Only a small quantity of a solidifying substance (m.p. 100-105°) was obtained after a large prefraction of b.p. 240-280°C. Therefore we tried to react the monochloride with methanol in pyridine. The reaction product was taken up by water. A voluminous precipitate resulted which, upon recrystallization in methanol, gave a substance which did not even melt at 250°C. It was not studied further.

We now heated to boiling 15 g. monochloride with 1.5 g. methylalcohol in ether for 2 hours. The ether was steamed off. The solidifying residue was recrystallized twice in petroleum ether. The m.p. was 131-132°C. The ester is easily soluble in the usual solvents (benzol, ether, alcohol, chloroform). A slight acid reaction was still present because of traces of monochloride.

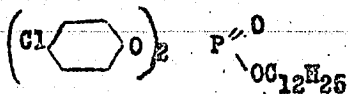
34.34 mg substance, Curious, 30.22 mg AgCl
found Cl = 21.7% calculated Cl = 21.3%
17.48 mg substance, 5.05 mg H₂O, 21.70 mg CO₂
C₁₃H₁₁O₄Cl₂P (353) found H 3.2% C46.3%
calculated H 3.3% C46.8%

17. Di-p-chlorophenylphosphoric acid propyl ester



Attempts to obtain this ester from the Na salt of di-p-chlorophenylphosphate and propylbromide in absolute alcohol failed. Neither did we obtain good results with the use of monochloride sodium and excess propyl alcohol. After that we used only the exact calculated quantity of propanol, monochloride and sodium and allowed them to react in benzol. 4.6 g. sodium was brought to react with 11.9 g. propanol and 80 cc benzol by heating it and blowing through of H₂. After cooling we added dropwise 56.8 g. monochloride in 100 cc benzol. It was heated for 3 hours under reflux. It was shaken with water and the salt solution separated in a separatory funnel. The benzol layer was dried with sodium sulfate and the benzol was finally steamed in vacuum. The remaining oil solidified in the icebox and was recrystallized three times with petroleum ether until the melting point remained constant at 113.5-114.5. The substance was neutral.

18. Di-p-chlorophenylphosphoric acid lauryl ester



4.6 g. sodium was covered with 50 cc of dry xylol and a solution of 37 g. lauryl alcohol in 100 cc xylol was dropped in slowly at room temperature. Meanwhile dry H₂ was conducted through. Then it was heated at the boiling point of xylol under reflux until all the Na had reacted. That was after about 5 hours. Under cooling in ice water we dropped 40 g. monochloride in xylol into the sodium laurate. Upon heating the reaction occurred. The solid laurate went into solution. No NaCl formation could be observed. It was heated to boiling for one hour, the xylol was steamed off and the residue taken up by ether. The ether solution was shaken with water and in order to remove di-p-chlorophenylphosphoric acid that may be present, it also was shaken with soda solution. We dried with sodium sulfate, steamed off the ether and drove off the remaining xylol in a vacuum. The remaining oil solidified soon. The ester is readily soluble in ether, benzol, glacial acetic acid, chloroform, acetone, ethyl acetate and pyridine, less readily soluble in alcohol and petroleum ether, insoluble in water. The product recrystallized in petroleum ether had a m.p. of 95-100°.

19. Phosphorus trichloride

PCl₃

We needed a large amount of PCl₃ for the production of S-containing substances. A series of methods have been worked out for its production. Even if one considers only newer investigations that require PCl₃ as auxiliary substance, various methods are used. One can see from that that no ideal laboratory solution has been found until now. First it was prepared by Serrulas (51) out of H₂S and PCl₅. He was followed by Wöhler and Hiller (52) who reacted sulfur monochloride with white P. Both methods were used later, but as mentioned in the beginning, they are not very convenient. Flemming (53) purified the product obtained by Wöhler's method by shaking it with water. Pletz (54) dissolved PCl₅ in CS₂ and conducted H₂S into it. Baudrimont allowed PCl₅ to react with antimony trisulfide. The removal of SbCl₃ caused difficulties. Simon (55) also used this preparation method. Other authors used reactions in sealed tubes. Henry (56) heated S and PCl₃, which compounds do not combine at the temperature of boiling PCl₃, in a tube at about 130°C, and he obtained a quantitative reaction. We repeated his experiment but we obtained very varying results even when we raised the temperature. Sometimes complete reaction occurred, sometimes the components were recovered unchanged and at times the reaction was incomplete. By adding of 10% dry H₂S as suggested by Woodstock and Adler (57) and by keeping the temperature between 150-160°C we always obtained quantitative results.

Thorpe (58) melted P₂S₅ with PCl₅ also in the tube and Bruno de Faze (59) worked under the same conditions with P₂S₅ and CCl₄.

All these methods had the disagreeable features and time losses that are always connected with working in sealed tubes. The new commercial production methods start with ferro-phosphorus and sulfur chloride (60). The l.g. (61) has recently worked out a method in which PCl₃ vapors are conducted into sulfur that is heated over 140°C but not over 160°C. I simplified this process for the laboratory by dropping PCl₃ into the heated sulfur while stirring. The yield corresponds about to that attained by l.g. with PCl₃ vapor. The l.g. obtained 205 g. PSCl₃ from 250 g. S and 500 g. PCl₃ after a reaction time of six hours. The boiling point was 118-122°C. We heated 400 g. S in a flask with 3 necks to various temperatures and let 250 cc PCl₃ drop in. The dropping time was also varied. The sulfur was stirred vigorously, whereby a KPG stirrer was of great service. The mixture of PCl₃-PSCl₃ distilled off immediately at 80-115°. It was fractionated afterwards and the recovered PCl₃ was used again. For the apparatus see Figure 3.

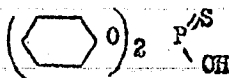
Experimental Results

<u>Nr</u>	<u>Duration of dropping in hrs.</u>	<u>S Temperature °C</u>	<u>Yield g</u>	<u>= % of theoretical yield calc. as PCl₃</u>
1	7	190-200	160	52
2	3	190-200	85	27.2
3	4	190-210	95	30.4
4	4	160-170	50	16.2
5	4	240-250	85	27.2
6	4 (4 times the total amount was dropped in.)	200-210	65	21.1

The series of experiments shows that the temperature used by I.G. of 140°-160° is not enough when PCl₃ is dropped in. I.G. states that the temperature chosen by them is particularly favorable since S becomes too viscous when heated above 160°. In my tests I found that the viscosity of the molten sulfur did not cause any difficulties up to 250°C when a glass stirrer was used. We found, as far as one can tell from such a short series, 190-210°C as the optimum temperature. Higher temperatures shorten the residence time of phosphor trichloride apparently too much. For laboratory purposes the last method seems to be the most convenient.

20. Diphenylthiophosphate

Beilstein 6/181 (96)



According to Athenrieth and Hildebrand (62) 3 mols. of phenol (57 g.) were dissolved in 120 cc of 20% NaOH and 1 mol. PSCl₃(33g.) was added. That was heated for 2 hours on a water bath. The oily layer is taken up in ether, dried with sodium sulfate and the ether is distilled off. The residue solidifies in the cold and was recrystallized with alcohol. The melting point was (K) 53°, the yield 40 g.

S determination according to Carus:

37.90 mg substance 26.72 mg BaSO₄
 found S=9.7%

 Calculated S = 9.8%

1 mol. of thiophosphate was heated with 1 mol. NaOH (alcoholic, since aqueous NaOH cannot be used according to Athenrieth) for 2 hours on a water bath. The solution was steamed dry, the residue dissolved in sodium carbonate and the phenol was removed with ether. The watery layer was acidified and again extracted with ether. After drying and vaporization, the ether layer left behind a yellowish oil that could not be distilled in the vacuum without decomposing. It was diphenylthiophosphate.

21. Di-p-chlorophenylthiophosphate

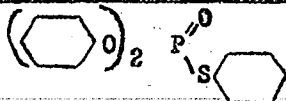
The neutral ester was obtained like the diphenylthiophosphate according to Authenrieth and Hildebrand (62), but not crystallized. Then it was hydrolyzed with ethylalcoholic NaOH. A dark oil was obtained.

64.53 mg substance 101, 31 mg CO₂

found C = 43.8%

calculated C = 43.0%

Strecker and Grossmann (65) doubt that tri-p-chlorophenylthiophosphate was obtained that way. It is true that Authenrieth obtained also the analogous triphenylthiophosphate with correct constants.

22. Diphenylphosphoric acid thiophenyl ester

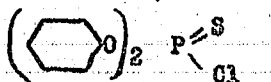
For the production of this ester we put together calculated amounts of diphenylphosphoric acid monochloride and thiophenol. No reaction occurred at first, but it started immediately after pyridine was added. It was heated for 6 hours and then the pyridine chloride was dissolved out with water. Then we washed with dilute HCl (pyridine), with Na₂CO₃ solution, and finally with pure water and we dried with sodium sulfate. During distillation in CO₂ flow the following fractions resulted:

1. Prefraction b.p. 15 60-64° (about 10 drops)
2. Prefraction b.p. 30 245-275°
3. Main fraction b.p. 23 275-282°

Upon rectifying the ester was obtained in the form of a colorless oil with a b.p. 288°-290°. This ester was not known yet but its isomer, triphenylthiophosphate was.

23. Diphenylthiophosphoric acid monochloride

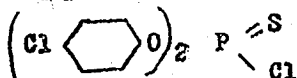
Beilet. 6/181 (96)



Phosphorous acid phenyl ester monochloride served as starting material. That was obtained in the procedures according to Noack (63) and according to Anschütz and Emery (64) from phenol and phosphorus trichloride. In the vacuum distillation of the reaction product in a CO₂ current the chloride passed over at b.p.₁₁ 172°. Then the chloride was heated to 190-200°C for a short time with the calculated amount of flowers of sublimated sulfur according to the process of Anschütz and Emery (18) Strecker and Grossmann (65). Simultaneously CO₂ was conducted through. The reaction product, a brown mass, was vacuum fractionated. The product (b.p.₁₁ 193-194°) obtained thereby was contaminated somewhat by sulfur and therefore was colored yellow. It was obtained pure by recrystallizing it from hexane.

24. Di-p-chlorophenylthiophosphoric acid monochloride

Bellat 6/188 (107)



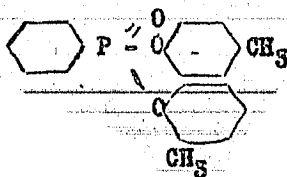
First it was attempted to prepare this chloride from sodium-p-chlorophenolate and phosphoric sulfochloride in xylol, but we obtained only 5 g. of the described thiochloride from 50 g. PSCl₃ and 84 g. phenolate. Therefore we prepared it in analogous manner to preparation 23. First we heated 2 mols. (238 g.) p-chlorophenol of b.p. 210-217° with 1.5 mols. (206 g.) PCl₃ with conducting through CO₂ for 1-1/2 hours under reflux. Then we fractionated immediately.

130 g. Prefraction and dichloride	b.p. ₁₂	0°-207°
135 g. Monochloride	b.p. ₁₀	207°-235°
40 g. triphosphite	b.p. ₁₀	270°

Preexperiments in which a large excess of PCl₃ was used (according to directions of Strecker and Grossmann (65)) gave only negligible quantities of monochloride (1 mol. chlorophenol + 2 or 3 mols. of PCl₃).

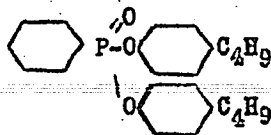
115 g. monochloride were heated with 11.5 g. of S to 250°. The reaction occurred with formation of heat and it turned brown. The obtained oil was fractionated in a vacuum. After a small prefraction came the main quantity (120 g.) at b.p.₁₂ 230-260°. After a few days the chloride solidified spontaneously. ~~It was filtered with suction and washed with a little ether.~~

25. Phenylphosphinic acid dimethyl ester



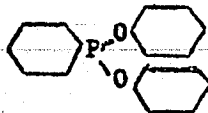
This ester was prepared like the phenyl ester. Phosphorylchloride served as starting material and a mixture of the three isomeric cresols in ratio 1:1:1. Upon mixing of the components a violent reaction and vigorous HCl development occurred. It was stirred for 2 hours and then it was distilled. After a short prerun, the ester came off at b.p.₂₈ 255°-278° most of which came between 270°-272°. From 55 g. of phosphorylchloride and 100 g. cresol 55 g. of ester were obtained, that is, 53% of the theoretical yield. The ester did not solidify even at cooling to 0°C. The boiling point at normal pressure was b.p.₇₆₀ 390-400°.

26. Phenylphosphinic acid di-p-butylphenyl ester



This compound was prepared by the addition of 17 g. butylphenol to 6.7 g. phosphorylchloride that had been chlorinated. The butylphenol was prepared from p-butylbenzolsulfonic acid by alkaline fusion. It was stirred for 4 hours to complete the reaction and then fractionated in a vacuum. After a short prefraction came the main portion at 260°-318° at 20 mm Hg, most of that between 305-318. The yield was 12 g = 78% of the theoretical yield. The ester, an oily liquid, is considerably less viscous than preparation 25 which is particularly noticeable in the cold.

27. Phenylphosphinous acid diphenyl ester



This substance that has not been described so far is readily prepared by heating phosphorylchloride and phenol. One heats 50 g. phosphorylchloride with 88 g. phenol for 3 hours on a sand bath, keeping the temperature between 150-170°C. Then it is distilled. First the prefractions and the excess phenol came off. At b.p.₁₅ 217°-228° the desired ester passes over. After the rectification, it boils at b.p.₁₅ 225-228°C. The yield was 70 g. = 85.5% of the theoretical yield. After a few days the ester solidified to a colorless crystal substance. 234.85 mg. of substance gave 90.85 mg Mg₂P₂O₇ (Carins). Calculated P = 10.87% found P = 10.8%.

III. Improvement of the Oil Solubility of the Additives

An insufficient solubility in mineral oil was first noticed in the case of diphenylphosphate. Therefore it was attempted to raise it through a suitable solubility promoter. That substance had to be chosen so that it would not impair the properties of the lubricant. That put great demands to its thermal behavior.

The task was to bring about the solution of a polar compound, the diphenylphosphate, in a largely unpolarized mixture, the mineral oil. After several experiments, we came upon lauryl alcohol. Lauryl alcohol has a relatively high boiling point, is soluble in oil and dissolves diphenylphosphate readily. This favorable behavior is to be traced to the structure of its molecule. On the one hand lauryl alcohol contains the polar hydroxyl group, on the other the lipophile dodecyl part. Particularly favorable for some practical experiments was the fact that a solution of 1 part diphenylphosphate and 1 part lauryl alcohol form a homogenous liquid after heating it to 120°C to drive out the water of crystallization of the diphenylphosphate. This simplified the addition of the admixture considerably.

The following is an abstract of various solubility tests:

Oil	Admixture (Diphenyl- phosphate)	Solvent Mediator		Heated to °C	Stood at °C	Condition
		Com. Lauryl Alc. of D.	Hy. W.			
Shell AB 11	0.6%	-	-	150	20	Turbid
"	0.6%	-	-	150	-15	Very turbid
"	0.6%	1.0%	-	150	20	Nearly clear
"	0.6%	1.0%	-	150	-15	Slightly turbid
"	0.6%	2.0%	-	150	20	Clear
"	0.6%	2.0%	-	150	-15	Nearly clear
Essolub 40	0.3%	-	-	120	20	Slightly turbid
"	0.2%	-	-	120	20	Clear
"	0.6%	0.5	-	120	20	Clear
"	1.0%	1.2	-	120	20	Clear
Rotring	0.3%	-	-	120	20	Clear
"	0.5%	-	-	120	20	Slightly turbid
"	1.0%	-	-	120	20	Very turbid
"	1.0%	0.7	-	120	20	Clear
"	1.2%	1.5	-	120	20	Clear

Also for the I.G. Farben preparation 891 lauryl alcohol had a similar effect. Later the object was to stir the preparations into the oil without heating. Thereby Dr. Brockstedt determined for 1586/80 I.G. that it can be stirred in the cold in a mixture ratio of 1586/80:benzol:alcohol as 2:1:1. According to our experiments the preparation also does not separate out in flakes when kept at -18°C for 3 days.

~~In order to incorporate the phenylphosphinic acid diphenyl ester into the oil in the same convenient manner we tried a number of solvents. Experiments with benzol, toluol, carbon tetrachloride, ethanolbutanol, methylethylketone and others failed. Only the combination ester:benzol:ethanol in the ratio 4:3:3 was successful. This mixture, a thin liquid oil, can be stirred into "Rotring" in the cold without reprecipitating at -15°.~~

Later it was tried to avoid the use of solvent mediators and solvents by building corresponding group into the molecule that would make it lipophilic. This was accomplished for the two preparations for which it was attempted. By reacting phosphoryltetrachloride with p-butylphenol or resp. a mixture of the 3 isomeric cresols phenylphosphinic acid di-p-butylphenyl ester and phenylphosphinic acid dicresyl ester were prepared. Both of them are clear liquids that can be admixed to the oil at room temperature in 2 concentrations of 1.5%. It was not attempted to prepare higher concentrations.

The same process was used for di-p-chlorophenylphosphate. Derivatives with one methyl, propyl, butyl, amyl, and lauryl group in the nucleus were prepared. As preliminary result we note that Di(2 chloro 4 butyl phenyl)-phosphate can be mixed with "Ligroin" in the ratio 1:1 while di-p-chlorophenylphosphate is only soluble to 0.07% in the same solvent. These experiments are still carried on and completed by "r. Fischer in the frame of a diploma thesis.

It was shown that solvent mediators were practical in the preliminary tests but that the preparations that were finally used had to be made oil-soluble by introducing lipophile groups. That was particularly desirable because of possible storage for a long period of time.

IV. Study of the Oils Containing Additives

The lubricants were tested carefully through the use of various methods of examination. One cannot get along without an oil testing machine when testing so many preparations, since motor tests would require much time and material and yet they would not give sharp differentiations. It was found that the results obtained with the Siebel-Kehl wear testing machine were in close agreement with those obtained on the bearing testing stand and in motor tests. The following testing installations were used:

- (a) Siebel-Kehl wear testing machine
- (b) Bearing testing stand
- (c) Driving tests in 2l BMW car
- (d) Tests in airplane motors
- (e) Tests in four ball apparatus
- (f) Ring sticking test and other lubricant tests

(a) Testing with the Siebel-Kehl wear testing machine carried out by Dr. Brockstedt of the State Material Testing Institute at the Technical University Stuttgart.

This machine worked only with sliding friction. The scheme of the testing arrangement that was described in detail in my diploma thesis can be seen in Figure 15. Also the dimensions of the testing bodies are recorded there. They are in a lubricant bath that is kept at a constant temperature of 120°C. They run with their faces against one another. In order to attain high plane pressure, the lower stationary test piece has segment-shaped openings. The total contact area is 33 square mm. The lower stationary parts are made of normalized (glowed?) steel St60.11. The upper parts consist of piston alloy EC 124 respectively lead bronze or silver. For a sliding velocity of $v = 1$ m/sec. a course of 2.0 km was chosen for each test and stage of load. That corresponds to about 1/2 hours. The moment of rotation was constantly recorded and therefrom the friction value was calculated. Before starting each series of experiments, the surfaces were carefully wiped (lapped?) and ran first with a plane pressure of 120 kg/square centimeters. Then it was taken apart, cleaned, the pieces ground off were determined and finally it was reinstalled with fresh oil. In intervals of 2.0 km of course the loads were increased up to corrosion (steep increase in friction values) of the slide planes, without taking the testing parts apart (between loads). Figure 16 gives a complete picture of the machine. Figures 23-25 show the effect of the admixture of phosphorylchloride.

Results

The following tests were all carried out with the material combination steel and EC-124. Where the optimal concentration had been determined for a preparation through a series of experiments an "O" is placed after the concentration percentage. Rotring was used as the oil throughout.

No.	Admixture	Conc.	Highest load endured	Friction value		Remarks
		%		Start	End	
	Pure oil (Refining)	"	150	0.08		
	Dibutylphosphite	1.0	450	low		
7	Diphenylphosphate	1.0 (o)	750-1000	<0.01	<0.01	+1% lauryl alcohol
1	Phenylphosphinic acid di-phenyl ester	1.2 (o)	600-1000	0.02		
4	Phenylphosphine acid mono phenyl ester	1.0	450	low		
2	Phosphoryl chloride	0.1 (o)	850	0.01	0.01	
36	Phosphorylous acid	0.5-0.4 (o)	750	0.01	0.01	
38	891 I.G. Farben	0.8 (o)	750	0.01	0.01-0.02	
	1534 I.G. Farben	1.0 (o)	450	0.04	0.08	
9	Di-p-chlorophenylphosphate	1.0 (o)	71400	<0.01	<0.01	
9	Di-p-chlorophenylphosphate heated 1 hr. 200°	1.0	71400	<0.01	0.02	
15	Diphenylethyl phosphate	1.6	550	0.025	0.025	
49	Tricresyl phosphate + oleic acid	1.5 } 1.0 }	450	0.02	0.02	
50	Tri-p-chlorophenyl-phosphate	1.0	150	0.08		
12	Di-2,4-dichlorophenyl-phosphate	1.0	500	0.02	0.08	
32	Diphenylchlorophosphine	0.4-0.5 (o)	950	0.01	0.01	
6	Isopropylbenzoldichloro-phosphine	0.5	750	0.01	0.02	
10	Dicresylphosphate	1.0	350	0.015	0.06	
48	Triphenylthiophosphate	1.0	150	0.08		
22	Diphenylthiophenyl-phosphate	1.0	180	0.06	0.08	
16	Di-p-chlorophenylphosphoric acid methyl ester	1.0	1400	0.02	0.02	contaminated with chloride
	"	0.5	850	0.01	0.01	
10	Di-p-bromophenylphosphate	1.0	1100	0.01	0.02	
21	Di-p-chlorophenylthio-phosphate	1.0	1050	<0.02	<0.02	
20	Diphenylthiophosphate	1.0	800	<0.02	<0.02	
8	Di-p-nitrophenyl-phosphate	1.0	550	0.02	0.08	
17	Di-p-chlorophenyl-phosphoric acid propylester	1.0	1400	0.02	0.02	contaminated
	"	1.0	150	0.08	0.08	purified
18	Di-p-chlorophenylphosphoric acid lauryl ester	1.0	150	0.04	0.08	
14	Di-p-chlorophenylphosphoric acid mono chloride	1.0	950	<0.01	<0.01	
11	Di-p-fluorophenylphosphate	1.0	1400	0.01	0.01	

Y	Admixture	Conc.	Highest load endured	Friction value		Remarks
		%		Start	End	
3	Phenylphosphinic acid di-p-chlorophenylester	1.0	500	0.04	0.06	
5	Phenylphosphinic acid mono-p-chlorophenylestermono-chloride	1.0	650	0.02	0.02	resinified
23	Diphenylphosphoric acid sulfochloride	1.0	300	0.03	0.04	
24	Di-p-chlorophenylphosphoric acid sulfochloride	1.0	550	0.04	0.07	
	Phenylphosphoric acid di-phenyl ester chlorated	1.0	450	0.04	0.07	
42	Sulfur	0.008	450	0.10	0.14	X
41	Diethylamine-N-sulfochloro-phosphine	1.0	150	0.08		
40	Monoethylaniline-N-oxi-chlorophosphine	1.0	200	0.04	0.08	
25	Phenylphosphinic acid-diocresyl ester	1.5	850	0.02	0.08	
26	Phenylphosphinic acid di-p-butyl phenyl ester	1.5	750	6.04	0.09	
27	Phenylphosphinous acid-diphenyl ester	1.0	900	0.04	0.04	
	Essolub 20 pure		120	0.13		
	Essolub 40 pure		120	0.10		

X Higher concentrations were also tested. They showed worse behavior. Tests with lower concentrations are in progress.

Without effect were:

- a. Diphenylphosphinic acid. The solubility is too poor.
- b. Oxiphosphazobenzolanilid (0.5%).
- c. Rings prepared with diphenylphosphate in xylol.
- d. 3% salicyl acid methyl ester (for sale by Schuchardt, Gorlitz) which was named by Evans and Elliot(141).
- e. 2% benzolsulfochloride, that was patented by the Gulf Oil Co. (142). The preparation was prepared from benzolsulfonic acid according to Gattermann (143).
- f. Naphthalin tetra chloride patented by Evans, prepared from naphthalene according to Schwarzer (145).
- g. Chlorinated diphenylsulfide in 1% solution, reported by the General Electric Co. (146), prepared from diphenylsulfide (146).
- h. Monochlorothianthren prepared by Fries and Vogt (147).
- i. Diphenylsulfide prepared according to Hartmann, Smith and Dickey (148).

b. Bearing testing experiments in the machine laboratory of the T.H. Stuttgart, Research Institute for Heat Engines. (Prof. Wewerka).

This test shows much larger dimensions than the Siebel Kehl machine and leads over to practical use. There is a picture of the machine in the report by Wewerka (138). Vath (139) gives a scheme of the testing arrangement. The machine can be loaded up to 10 tons so that one obtains pressures up to 1000 kg/square centimeter. The loading occurs hydraulically by two oil pistons. The bearing diameter is 45 mm., the length 20 mm. At 3000 rotations of the driving motor the sliding velocity amounts to 7 m/sec. The test roll is made of nitrided steel and is ground and lapped. The diameter play of the bearing is 0.09 mm (see Fig. 17). The bearing casing material can be changed each time. When the maximum load is reached the temperature in the bearing rises considerably and the machine is turned off to save the drive motor.

Wewerka and associates found that the specific carrying capacity increases periodically with the lubricating oil pressure and indeed in a wide area with $\frac{1}{p}$. Therefore a straight line curve results when plotted on double logarithmic paper. This makes a control of the exactness of the experiments possible (Fig. 18). We have used it also in the experiments with our preparations. The following results were gotten in the tests.

The table contains the specific carrying capacity of various materials with a lubricating oil pressure of $p = 1$ atmosphere absolute pressure and the above test conditions.

Lubricating oil

EC 8 4.5° Engler/50°C

	Lead bronze		Silver		Special brass		Light metal	
	kg/30.cm.	%	kg.	%	kg.	%	Manila	%
pure	270	--	390	--	300	--	500	--
0.05% Phosphenylchloride	290	--	500	28	140	53	--	--
0.3% Phosphenylous acid	450	65	740	90	350	17	200	17
0.6% 891 I.G. Farben.	410	52	1200	210	440	47	780	30
1.2% Phenylphosphinic acid diphenylester	780	188	470	21	1000	230	760	27

* The % figures were stricken out in the original

The figures show the presence of far-reaching agreement with the results of the Siebel-Kehl machine. Fig. 18 shows the dependence of the load upon the oil pressure. Fig. 19 shows the effect of the additives on the bearing temperature. The final temperature at reaching the terminal load (critical bearing temperature) is equally high for the various additives. The effect on the carrying capacity varies clearly for the various materials.

c. Driving tests in a 2 BMW auto car carried out by Prof. Glockner, Inst. for Metal Physics at the Kaiser Wilhelm Institute for Metal Research, Stuttgart.

A considerable diminution of effectiveness could be determined in the heating experiments on oils with additives. Endurance tests on the Siebel-Kehl wear testing machine at 126°C and on the bearing test stand showed a small decline. Driving tests were carried out in a 2 BMW car in order to clarify the conditions which are very important in practical use of the motor. Oil was drawn before start of the drive and after certain intervals and it was tested on the Siebel-Kehl machine. Thereby the effect ~~decreases rapidly in the beginning and then it declines gradually~~ (Fig. 6 and 7). The named driving distances are covered without adding fresh oil. A replenishment of the additive (Fig. 7 and 8) restored the starting effectiveness which declined again.

In judging of the lubricant oil the friction value and the endured plane pressure were considered. That is the pressure at which no corrosion of slide surfaces yet occurs. Declining values in surface pressure and increasing friction values indicate decline in effectiveness. But one must observe that for some admixtures also with small endured pressure the friction value remains nearly unchanged up to the corrosion point (diphenylphosphate).

It is not quite clear yet whether the decline in the effect is caused by a reaction of the additive with the lubricating oil or with metal parts that are to be lubricated. (see introduction). Purely thermal decomposition, which can only be considered on a large scale in the close vicinity of the combustion zone, does not seem to be the decisive factor. The thermal endurance of the best additives reach that of the lubricating oil proper.

Experiments with a stationary single cylinder NSU motor 201 that were carried out in the Research Institute for Automobiles, Stuttgart (Prof. Kamm), gave an analogous picture (Fig. 9).

d. Experiments with airplane motors carried out by Daimler and Benz Factory.

The conditions in the airplane motor are more favorable than those in the automobile motor because in the airplane motor oil must be replenished from time to time. Therefore, the declining values of the surface pressure could not go below a constant middle value. In the automobile engines, oil is changed only at very long intervals. The results of the experiments with the different additives are presented.

The starting effect is not retained completely in Fig. 10-14 in any of the three admixtures examined.

A decline to $p \approx 350$ kg./square centimeter occurred after about 5 hours in the complete motor for diphenylphosphate. This value does not decline further in continued operation. The endured pressure for Rotring oil without additive amounts to about 150 kg./square centimeter, and considerably higher friction value.

Phenylphosphinic acid diphenyl ester gave already after 3 hours a mean pressure value of 325 kg./sq. centimeters (Fig. 11 and 12). The friction value rises with the decline of the endured pressure and in the most unfavorable case it amounts to 0.07. The friction value of diphenylphosphate remains at 0.025.

The decline in effect in the single cylinder motor (Fig. 11, 13, 14) proceeds much more slowly than that in the complete motor, which can probably be traced to the higher thermal demands in the latter.

In admixture 891 there was a slight rise in effectiveness after the initial decline. There resulted a mean surface pressure of 500 kg./sq. centimeter and a friction value of 0.025. The new rise occurred after the first addition of a quantity fresh oil.

Test series with I.G. Farben 891 showed the effect of this preparation at the run-in. The corrosion of bearings that otherwise required much consumption of time did not occur.

e. Testing on the four ball apparatus of Boerlage
 carried out by Ober Ing. Glaubitz at the State Material Texture Institute,
 T.H. Stuttgart.

The tests with sulfurized oils (also gear oils) showed little or no improvement on the Siebel-Kehl machine as compared with the four ball apparatus of Boerlage or in highly loaded gears. In order to obtain comparability and further testing opportunity but particularly in order to test the possibility to use our preparations as gear oils the tests on the four ball machine were carried out (suggested by Dr. Brockstedt).

The four ball apparatus was developed by Boerlage (135) in 1933 for Rataafsche Petroleum Maatschappij in Delft to test extreme pressure lubricants. Its particular advantage is the use of steel balls as testing bodies. They are cheap and can be obtained in otherwise not attainable regularity. In the course of years it was proven that the values obtained in this experimental arrangement agree closely with the conditions as they occur in gears and other cog-wheel lubricating points. (see also Seemann) (136).

The apparatus was retested and tried by Rhenanie-Ossag (136) and later by DVL (137). Four pyramid ally-arranged steel balls served as friction elements (Fig. 4). Three of them are fastened to the test vessel by a clamp ring and a screw cap. In this vessel is also the lubricant to be tested. The fourth ball is clamped tight by a chuck which is firmly connected with a spindle to the shaft of the drive electro motor. (Fig. 5). The casing that carries the motor can be loaded by means of a lever and it passes the load on to the lubricating spots. The occurring friction moment is measured by means of an indicator spring.

In the tests at the Material Testing Institute, steel balls or phosphated steel balls were used. The use of BONDORIZED (phosphated) steel balls followed preliminary experiments by the Daimler-Benz A.G. (Dipl. Ing. Bokemuller and Dr. Seemann). The balls always run one minute with a certain load. Then they were dismantled, cleaned and the wear calottes (a flattened dome) were measured. One measures in the running direction and the direction at right angles to it. One plots the average value of the 3 balls against the load. The fourth ball shows a circular wear ring. That is not taken into further consideration. The point of corrosion is the point at which a sudden increase in friction and wear occurs. (Fig. 5a). At the melting point the balls are welded together tightly. Other concepts like point of elasticity, point of activity were not considered since they need to be clarified yet.

Results of Four Ball Apparatus
(steel balls)

Kind of oil	Admixture %	Corrosion point load kg	Welding point load kg
Rotring	--	110	180
MOWS	--	100	200
Essolub E 20	--	110	180
MOWS	+1% Diphenylphosphate	160	200
"	+0.8% 891 I.G.	140	190
"	+0.5% 1455 I.G.	120	160
"	+3.0% 1534 I.G.	140	220
Rotring	+0.8% 891 I.G.	160	220
"	+0.3% 1455 I.G.	110	200
"	+3.0% 1534 I.G.	150	200
"	+1.0% Diphenylphosphate	170	200
"	+1.0% Lauryl alcohol		
"	+0.5% 14/135 I.G.	130	180
"	+0.5% 14/104 I.G.	150	180
"	+0.1% Phospheny chloride	150	180
"	+0.4% Diphenylchlorophosphine	110	180
"	+1.5% Triphenylphosphine	110	180
"	1.0% Tristearine		
"	+1.0% Tristearine	90	200
"	+1.5% Triphenylphosphate	110	180
"	+1.0% 100 M	210	260
"	+0.4% M 100	190	200
"	+1.5% M 100	230	280
"	+1.0% M 100 heated 1 hr at 200°C	200	240
"	+1.5% Phenylphosphinic acid diphenylester	90	180
"	+0.5% 1536 I.G.	150	170
"	+1.0% 401	190	240
Hypoid oil	sulfurized	~1000	~1000

Steel Balls Bonderized

Kind of oil	Admixture %	Corrosion point load kg	Welding point load kg
Rotring	--		340
MOWS	--		300
"	+1% Diphenylphosphate		600
"	+0.8% 891 I.G.		700
"	+0.5% 1455 I.G.		700
"	+3.0% 1534 I.G.		650
Rotring	+0.8 891		700
"	+1.0 Diphenylphosphate		
"	1.0 Lauryl alcohol		600
"	1% M 100	850	950

f. Ring sticking and Aging tests, carried out by the Technical Testing Station of the I.G. Oppau (Dr. Penzig)

The phenylphosphinic acid diphenylester behaved less favorably than I.G. 891 in the ring sticking tests but better in the aging tests. One must remember that in the ring stick test one uses extreme motor conditions. On the other hand, the aging test cannot be simply transferred to motor conditions.

	Rotring			
	Without admixture	+0.6% 1586/80	+1.2% Ester	+0.6% 891
<u>Fresh oil</u>				
<u>Viscosity in centistokes</u>				
38°C	263.5	262.5	250.5	270.3
99°C	19.25	18.90	19.01	19.3
Conradson's test %	0.35	0.26	0.21	0.32
Neutralization No.	0	0.81	0.18	1.25
Saponification No.	1.01	1.58	1.72	1.46
<u>Used oil</u>				
<u>BMW number</u>				
	685	693	691	694
<u>Viscosity in centistokes</u>				
38°C	268.5	195.5	256.5	219.9
99°C	18.14	15.76	18.95	16.94
Conradson's test %	0.77	0.60	0.46	0.68
Neutralization No.	0.36	0.78	0.51	0.67
Saponification No.	0.03	1.35	2.64	1.98
<u>Aging test according</u>				
<u>Brit. - Air. - Ministry</u>				
Loss %	3.8	3.8	2.0	6.4
<u>Viscosity in centistokes</u>				
38°C	369.5	450	339.6	774
99°C	25.0	27.2	22.4	37.4
Thickening at 38°C %	41	71	29	195
Conradson's test %	4.59	2.49	1.24	3.44
Asphalt	0	0	0	0

5. Phosphorus Compounds that are Named in the Literature as Additives to Lubricants

It is noteworthy which materials have been used previously as lubricant additives. To make a better survey they have been divided into three classes:

1. Derivatives of phosphor acids
2. Phosphines
3. All other P compounds

I. P acid derivatives

Standard Oil Development Co.

A turbine oil with high flame and spontaneous ignition point, consisting e.g. of Tricresylphosphate.

Atlantic Refining Co.

Mineral oil plus up to 10% of an organic phosphoric acid triester that may contain aryl or alkyl groups are used as high pressure lubricants. The compounds can also be halogenated. Tests were made on a Timken test machine.

E.I. du Pont de Nemours & Co.

Acid esters of ortho, meta and pyrophosphoric acid, of phosphorous acid and of hypophosphoric acid and alcohols or phenols increase the effectiveness of pressure lubricants.

E.I. du Pont de Nemours & Co.

Aliphatic or aromatic esters of phosphoric acid are used as lubricants for high pressure. Acid esters are suited for normal pressures and temperatures, neutral esters for high pressures and temperatures.

Socony Vacuum Oil Co.

In order to prevent the corrosion of metal surfaces that consist of Cd, Ag, Cu, or Pb alloys, mineral lubricant oils are given an admixture of 0.1-1% triphenylphosphite.

Socony Vacuum Oil Co.

In order to prevent corrosion, Tricresylphosphites in quantities of 0.1-1% are added to mineral oil lubricants.

Socony Vacuum Oil Co.

0.05-2% of a Triarylphosphite are used as antioxidant for hydrocarbon oils.

Celluloid Co.

Lubricants made of mineral or vegetable oils are mixed with an emulsifying agent and a neutral ester of phosphoric acid. The ester contains at least one aryl group. Also esters of thiophosphoric acid can be used. The lubricants are particularly suited for high pressures and velocities.

Standard Oil Development Co.

Lubricating and insulating oils consist of an ester of phosphoric acid like tricresylphosphate to which an antioxidation agent has been added.

Standard Oil Co.

A mixture of mono-di-and tri-alkyl phosphites has been added to lubricating oil in order to prevent the corrosion of certain bearing metals.

Canadian Industries, Ltd.

Bearings were lubricated with aliphatic esters of phosphoric acid in order to prevent corrosion. The esters react with the surface of the bearing.

Continental Oil Co.

A small amount of a phosphoric acid ester of an aliphatic or aromatic thiophenol or thioalcohol is added to mineral oils.

Standard Oil Development Co.

Liquid organic esters of phosphoric acid (tricresylphosphate) are used as lubricating oil for precision apparatus.

A. Foulon

Phosphoric acid esters are used as corrosion-stable high pressure lubricants.

E.I. du Pont de Nemours and Co.

Admixtures to high pressure lubricants are made from Naphthenyl alcohol and derivatives of phosphoric acid like PCl_3 , $POCl_3$, PCl_2 , $PSCl_3$ etc.

Atlantic Refining Co.

Mineral oils obtain high pressure properties when compounds are added that are prepared of PCl_3 , PCl_5 , PSCl_3 , P_2S_3 , P_2S_5 with primary or secondary amines. (e.g. $\text{ClC}_6\text{H}_4\text{NHPOCl}_2$).

Standard Oil Development Co.

Lubricating oils and insulating oils become high temperature-stable through the addition of thio or seleno esters of phosphorous acid.

Standard Oil Development Co.

Admixtures of 0.02-5% of an organic thiophosphite gave high oxidation resistance to lubricating oils.

Socony Vacuum Oil Co.

Organic phosphites and thiophosphites improve mineral oils in their pressure properties and oxidation resistance. Hydrolysis is prevented by addition of amines.

Socony Vacuum Oil Co.

Admixtures of condensation products of PCl_3 and amines that have a free H atom on the N, prevent corrosion and give high pressure properties.

Curt Ehlers

Admixtures of tricresylphosphate to motor oils cause corrosion by the liberated phosphoric acid.

Standard Oil of California

Esters of thiophosphoric acid improve pressure resistance. (e.g. triamylthiophosphate).

C.M. Laron

Among other materials phosphates serve as oiliness admixtures for airplane motors. One gets separation of lead phosphate at the exhaust.

Standard Oil Development Co.

Mineral oils are reacted with 0.5-2% aralkyl phosphates or phosphites.

Standard Oil Co.

Highly refined oils are improved in their corrosion behavior by the addition of chloralkylphosphites (primary, secondary or tertiary). The chlorine shown is preferably in α position.

E.I. du Pont de Nemours & Co.

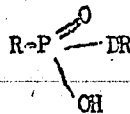
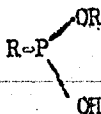
The corrosion effect of the oils on Cd-Ag alloys is prevented through the addition of alkyl, aralkyl and aryl phosphates.

Atlantic Refining Co.

In order to increase film tear resistance (elasticity) one can add aliphatic or aromatic phosphates, phosphites or thiophosphites to oils.

Standard Oil Co.

In order to reduce corrosion one reacts oil with phosphinites and phosphinates.



E.I. du Pont de Nemours & Co.

Mineral lubricating oils are improved with regard to corrosion, high pressure properties and sludge formation by the addition of naphthenyl esters of phosphorus acids. These compounds act better than the corresponding esters of the aliphatic alcohols and phenols.

General Electric Co.

Alkylphosphates are used in oil mixtures.

Gulf Oil Corp.

Oil-soluble phosphoric acid esters improve mineral lubricating oils for explosion motors.

N.V. de Bataafsche Petroleum Mij.

Lubricating oils are improved in their high pressure properties by the admixture of phosphoric acid esters of the structure $\text{R}-\text{O}-\text{P}(\text{Halogen})_2$. Thereby no corrosion occurs.

Standard Oil of California

Phosphoric acids substituted with metal salts improve lubricating oils in their heat resistance. They prevent the caking together of the piston rings.

Standard Oil Development Co.

The reaction products of phosphoric halogenides with olefines, or terpenes, etc. give high pressure properties to lubricating agents.

E.I. du Pont de Nemours & Co.

Film strength, lubrication power, corrosion resistance and oxidation resistance of lubricants are improved by the admixture of mono- di- or tri-esters of phosphorous or thiophosphorous acid. The acids are esterified with branched aliphatic alcohols of 6-9 C atoms.

E.I. du Pont de Nemours & Co.

The same improvement as in the previous patent occurs with addition of alkylthiophosphites whose alkyl groups are tied directly to the S atoms.

Atlantic Refining Co.

Lubricating oils are heated with 0.25-50% tricresylphosphites or another organic compound of 3-valent P. A part of the reaction products remains dissolved in the oil.

Gulf Oil Corp.

One reacts $POCl_3$ with alkylated phenols in the presence of small quantities of P_4S_{10} and one adds the products obtained that way to mineral lubricating oils. The high pressure properties, oxidation resistance and corrosion effect are improved and the covering with pitch of the piston rings is prevented.

I.G. Farben A.G.

Lubricants made of polymerization products contain tri-p-chlorethyl phosphate, tributyl phosphate, etc.

Lubri-Zol Corp.

One adds to mineral oils among other things metal salts of condensation products of triphenyl phosphate, triphenylphosphites, tricresylphosphates with substituted fatty acids.

Atlantic Refining Co.

Tricresylphosphate, butylphosphate and other esters serve as solution agents for admixtures of thio urea to lubricating oils.

Musher Foundation Inc.

One obtains lubricating oils with reduced corrosion and sludge formation by admixing 0.1-0.8% of a mixture of arylphosphites with lecithin and heating fairly long to at least 175°C.

Standard Oil Development Co.

Admixtures of 0.1-2% tertiary ester of phosphorous and thio-phosphorous acids to lubricating oils increase the lubricating, temperature resistance and oxidation resistance and reduce the tendency to contamination and C separation.

Texas Co.

Lubricating oils are improved by addition of tertiary olicyclic phosphites. The separation of di- and triphosphites occurs through vacuum distillation.

Standard Oil of California

One adds to mineral oils, metal salts of various P acids whose H atoms are substituted by various radicals.

Gulf Oil Co.

One obtains non-corroding, oxidation-resistant high pressure lubricating oils by addition of alkylphenolphosphite, thiophosphites and phosphates. The alkylphenols are prepared from olefines and phenols in the presence of sulfuric acid.

Standard Oil Development Co.

Admixtures of fatty acids and other materials like phosphites and phosphates improve mineral lubricating oils.

Texas Co.

Improved lubricating oils for combustion engines contain 0.01-2% Tri- Di- or mono-phosphite particularly of cyclohexanols.

Shell Development Co.

Preparations that are obtained by reacting PCl_3 and $POCl_3$ with tertiary alcohols, give high pressure properties to lubricating agents.

Standard Oil Development Co.

Phosphite esters of a certain configuration are used for the improvement of lubricating oils.

TideWater Associated Oil Co.

Mineral oils are stabilized through the admixture of 0.1-2% of a phosphite ester of thiophenol.

Richard Israel Levy

Castor oil is changed to oil soluble phosphoric acid ester by reaction with phosphoric halogenides and mineral lubricating oils are improved by the ester.

Walter G. Whitman

Alkylphosphates are added to improve lubricating oils in motors.

Monsanto Chemical Co.

Trihexylphenylphosphite and phosphate are used as admixtures for lubricating materials.

Standard Oil Development Co.

Tricresylphosphate is used for the preparation of compounded oil, besides other components.

Standard Oil Co.

Anti-corroding admixtures to mineral oil consist of alkyl or aryl mono-, di-, or tri-thiophosphites.

Ohio Oil Co.

Mineral lubricating oils obtain high pressure properties through the admixture of P-compounds up to 3%, such as butyllauryl or cresyl esters of phosphoric or phosphorous acid.

Lubri-Zol Corp.

Organic P-compounds (particularly esters of various P acids) serve as anti-corrosion agents in high pressure oils.

Lubri-Zol Corp.

Lubricating oils obtain high pressure properties by admixture of 0.1-2% halogenated aromatic thiophosphates that act at the same time anti-corroding.

Texas Co.

Mineral oils receive an admixture of a phosphite ester. The acid is esterized with alkyl ethers of alkyl glycols.

Canadian General Electric Co., Ltd.

A reduction of viscosity of oils is attained by adding 25-50% of an alkylphosphate. Thereby the alkyl does not contain more than 4 C atoms.

Celluloid Corp.

A steam turbine oil contains chlorinated diphenyl and about 50 parts of triarylphosphate.

II. Phosphines

N.V. de Bataafsche Petroleum Mij.

Complex compounds that contain inorganic components and e.g. tertiary phosphine (triethylphosphine) are suitable as admixtures to lubricating oils.

Atlantic Refining Co.

Mineral oils are improved in high pressure properties, lubricity, and friction coefficient by addition of phosphinic oxides and sulfides.

Atlantic Refining Co.

Admixtures of 0.1-5% organic phosphines give high pressure properties to mineral oils (tripyrilidyl phosphine, monophenyl phosphine, diphenyl phosphine).

Sun Oil Co.

Admixtures of propylbenzol phosphine and butylbenzoldichlorophosphine improve high pressure properties.

Atlantic Refining Co.

Tributylphosphine, triphenylphosphine, etc. can be used in place of triocetylphosphite.

Standard Oil Development Co.

To reduce sludge formation 0.1-5%, phosphines were added, triphenylphosphine, monophenylphosphine, tolyldiisobutylphosphine. The phosphines may contain also N, S, O, Cl.

Texas Co.

One uses admixtures of phosphinic acid esters.

Cities Service Oil Co.

Admixtures consist of condensation products of organic phosphines, or of chlorophosphinic oxides.

Standard Oil Co.

Triphenylphosphinic oxide and sulfide is added to oils to improve the corrosion behavior.

III. Other P compounds

Only short literature references are given.

As far as it is possible on basis of our experience, I should like to evaluate the foregoing patents briefly. I wish to observe beforehand that our development has proceeded first without paying attention to the patent literature. That was done because the results used there were attained on different test apparatus and therefore could not be compared with our results.

Neutral phosphoric acid esters that are mentioned showed no effect with us, the acid esters were effective. According to personal communication of Dr. Zorn (I.G. Leuna) to Prof. Glockner such esters (diphenyl phosphate) were introduced previously in the U.S.A. Air Corps. The tertiary esters and thiophosphoric acids will not be discussed further. It is stated that aliphatic esters react with bearing surfaces. We agree with that opinion when certain lubrication conditions prevail. The esters of thiophenol and alcohols did not give an improvement over oxygen-containing esters in our tests. The amines mentioned proved ineffective with us. The dihalogen mentioned are easily decomposed by H_2O and therefore not suitable. Phosphoric acids substituted with metal salts are generally insoluble in oil according to our experiments. It is noteworthy that the covering with pitch of piston rings is to be avoided by the use of esters. Phosphites which are mentioned several times were not very effective in our tests. Some of the phosphines mentioned probably do not give an improvement of high pressure properties. The dichlorophosphine is water decomposable in spite of the statement to the contrary. The phosphatides were not studied in detail by us. The pressure properties are improved by P heated with oil. But one obtains a dark oil and resinification. Phosphoric acid itself has no effect as we determined.

All in all there is a confusion of partly contradicting statements. ~~But one must assume that some preparations are in practical use in the U.S.A.~~ where most of them are patented. It is surprising that so little was worked with this here so far.

There follows a list of the illustrations, then the illustrations proper.

Fremos 114 to 118 List of References.

9/25/46