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THE PREPARATION OF PHOSPHORUS COMPOUNDS AND THEIR USE IN LUBRICANTS.

This paper deals with the synthesis of organic preparations containing phosphorus, their testing as regards suitability as additives to lubricants in oil testing apparatus and their testing in practical engine tests. The preparation and selection of the products was carried out in the Organic Chemistry Institute of the Technical College of Stuttgart, under the direction of Prof. Dr. E. Ott. Iam most indebted to him for the furtherance he has given to my work and for his constant support.

Inspiration for this paper was furnished by Prof. Glocker of the Inst. fuer Metallphysik at the K.W.I. fuer Metallforschung, Stuttgart. He also directed the tests and trials. Thanks to the fact that he merged chemistry, physics and machinery construction at the Technical College, the chemical and engine building industries, and the relevant departments of the Army into one working group, it was possible to continue the paper. I thank him for suggestions and advice which he always readily placed at my disposal. I must also thank Dr. Brockstedt, who showed great interest in the chemical side of the matter, and was ever most helpful to me both in conversations and by his own experiments. He also placed a large number of diagrams at my disposal. The requisite material was made available within the framework of instructions from the Research Directorate of the RdL and ObdL.

In collaboration with the Institut fuer Metallphysik at the KWI fuer Metallforschung, Stuttgart (Prof. Glocker)[1] the State Material Testing Institute of the Technical College, Stuttgart (Dr. Brockstedt)[2], the Research Institute for Heating Power machines of the Technical College, Stuttgart (Prof. Wewerka, Dipl. Ing. Dollhopf, Dipl. Ing. Hagmayer)[3], and the Daimler-Benz A.G., Stuttgart-Untertuerkheim (Dipl Ing. Anders), extensive trials were carried out. I have included part of the results in the paper for the sake of better comprehension.

The following also took part in the investigations: Prof. W. Kamm, Research Institute for Automobiles of the Technical College, Stuttgart:Tests with single cylinder engines. Mr. Obering. Glaubitz, State Material Testing Institute of the Technical College, Stuttgart: Tests with the four-ball apparatus. Dr. Widmaier, Research Institute for Automobiles of the Technical College, Stuttgart: Lubricant tests. I. G. Farbenindustrie A.G.: Lubricant tests, Testing Station Oppau, Dr. Penzig, work on allied preparations (Farbwerke III Leverjusen, Dr. Wahl). During work in the laboratory, expecially in making the preparations, some of whic were required in large quantities, Mrs. G. Loeckle and Miss R. Strobel have lent me active support, and I should also like to thank them here.

1) R. Glocker, Improvement to properties of bearings by additives to lubricants. Reports of the Lilienthalgesellschaft fuer Luftfahrtforschung, 170/34.

2) K. Wellinger and H.C. Brockstedt, Stability of the action of chemical additives in aero-engine trial runs, single cylinder and full scale engines. Test Report of 5.1.44.

3) A. Wewerka, Fundamentals and Results of slide bearing tests. Reports of the Lilienthalgesellschaft fuer Luftfahrtforschung 170 /38.

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1. Introduction

On the basis of a series of experiments (149) published by English authors, and with reference to investigations which Dr. H.C. Brockstedt carried out at the State Material Testing Institute of the Technical College, Stuttgart with preparations made by ourselves, it was first imagined that the addition of triphenyl phosphine would impart particularly valuable properties to mineral oils. It was said to decrease considerably the coefficient of friction and at the same time to add to the compressive resistance of the oil film. My diploma thesis then afforded proof that these properties are not to be attributed to the admixture of triphenyl phosphine itself, but to the presence of mixtures, mainly of monophenyl phosphine. Since monophenyl phosphine is easily oxidised in the air, it cannot be used for technical purposes. Phosphenyl chloride, which is similarly built up, and has been found very active even in quite small concentrations, is likewise unsuitable owing to other characteristics, such as low boiling point, readiness to be decomposed by water, and the separation of HCl.

The object of the present paper was to assess the knowledge thus gained and evolve preparations, which through their other behaviour were suited for improving lubricants with a mineral oil basis.

With this in view, further and more detailed research was conducted with phosphenylic acid, which had also been produced during my diploma paper, in spite of its poor solubility. As a direct derivative of phosphenyl chloride, it also gave promise of possessing the ability to combine improvements to the coefficient of friction and of the compressive resistance. Its activity also corresponded to the configuration, and a few other properties were likewise favourable, but the decomposition into monophenyl phosphine, benzene and metaphosphoric acid when strongly heated, prevented its use in the I.C. engine, where it was mainly required.

A number of properties are given below which should be possessed by an additive for oils of highly stressed I.C. engines (aero engines) in addition to its activity proper:

1. High temperature stability, if possible over 300°C.
2. Solubility in oil, making it possible to add suitable amounts to oil, if possible without heating. The additive must not be precipitated at winter temperatures. An improvement in solubility by suitable solvents is of course possible.
3. Corrosion of the materials to be lubricated must be kept within very narrow limits.
4. Insensitiveness to water and petrol containing lead.
5. No negative change in the physical properties of the oil (viscosity, pour point, flash point, foaming etc) and in the chemical lubricant tests (coking, ageing, neutralisation number etc).
6. Practically non-poisonous.
7. Storage stability
8. No increase in ring sticking
9. Practical synthesis and accesible raw materials.

As will be seen from the very large number of patents on this subject (expecially in the U.S.A.), the search for such a material is no easy one. Some help is afforded if the search for a universal additive is modified and the purpose of the material is somewhat limited. The absence of one or other of the points given above can thus be tolerated. Our interest has thus been directed mainly towards the running-in process, where some remedy was required for the seizing of bearings, a more frequent phenomenon. Since the engines are again dismantled after running in, some of the demands under 1-9 above need not be so rigorously applied. Furthermore, we concentrated on gear oils, where the oil bath temperatures are not so high. It should nevertheless be mentioned thatthe additives respond differently to changes in the combination of materials and in the oil, and this makes the selection again complicated.

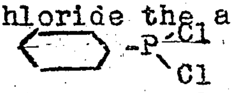
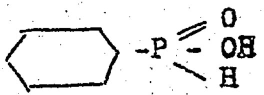
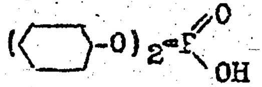
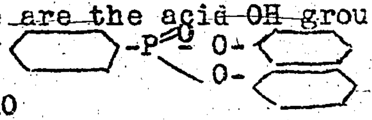
In seeking materials, which configuratively resemble phosphenylic acid, but are very much more resistant to temperature, I hit upon diphenyl ester phenyl phospinate, which may be distilled at a BP_{760} of 370-380°C practically without decomposition. It no longer carries a free OH group and its activity is also somewhat changed in a corresponding manner. These facts will, however, be referred to below.

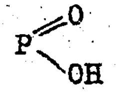
Owing to the considerable difficulty in manufacturing large quantities of ester, recourse was had to the similarly constructed substances of the more readily accessible phosphoric ester series. First of all diphenyl phosphate and later on dihalogenphenyl phosphates were examined, where the activity due to the introduction of the halogen in the para position was considerably increased. Sulphur derivatives were also included in the scope of the experiments. Since, however, with these acid esters the temperature stability was not quite sufficient, the OH group was reacted with an alcohol. The first figures obtained with the methyl ester were surprisingly good and could be attributed, after the preparation of the more easily soluble propyl and lauryl esters. to an admixture of monochloride. The di-p-chlorophenyl phosphoric monochloride will not, however, withstand temperatures above 280°. We next prepared the more temperature resisting phenylhosphinic monophenyl ester monochloride, which on being saponified, is changed into the equally active monophenyl ester. As a further improvement, the phenol nucleus was further chlorinated in the p-position. The preparation then produced utilisable figures, but involved undesirable resinification, which precluded its use. As the sulpho-chlorides are on the whole very much more stable against water than the oxy-chlorides, experiments were also carried out with di-p-chlorophenylphosphoric sulphochloride. This resulted in medium load capacities. An attempt to explain the connection between the various preparations will be made below. For the sake of completeness, however, it should be stated here that the IG, on the basis of our work, developed a preparation 891, which according to their data, represents a technical p-chloro-phenyl-phenylphosphinic acid. This preparation has been found good and can apparently be made on a technical scale. It nevertheless contains a free acid hydroxyl group.

The justificiation for using phosphorus compounds in particular as the basis for work in connection with high pressure lubricants has been clearly proved in the course of our experiments. Additives of other types of material, whether fatty acids, sulphur or chlorine compounds, frequently stated to be good in technical literature, have been tested by us on a comparative basis and yielded altogether inadequate results. Nevertheless neither these data nor those on the application of phosphorus compounds can be compared direct with our own, as they have been obtained on different test machines. All the same, after completing our work, we studied technical literature for additives containing phosphorus (v. part 5). The phosphines which chiefly occupied us during the diploma period, only took up a small portion of the number of references. The same applies to the phosphatides and inorganic compounds such as P_4S_3 and $PNCl_3$. Very much more space was devoted to the esters of the phosphorous and phosphoric acids. Here again the data do not agree with our check experiments. Thus, neutral phosphates, with or without sulphur in the molecule, produced neither increased figures for the pressure load nor reductions in the coefficient of friction. The substances will be found collated below.

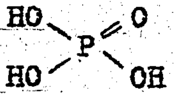
As to the cause of the activity of such additives, various explanations have already been furnished. Whereas Kern (150) lays stress on the formation of metal phosphate layers, Beeck, Givens and Smith (149) assume that the phosphorus of the corresponding compound is reduced and then forms low-melting phosphides with the sliding surfaces. These phosphides therefore prefer combinations with trivalent phosphorus in order to facilitate the reduction beforehand. On the other hand, we have always found in our investigations that compounds of pentavalent phosphorus possess excellent activity. Other writers, such as Wolf, Kluge, Frewing, Donandt, Trillat (151-155) devote their attention primarily to the adsorption (caused by polar groups) of the molecules concerned at the surface of the metal. Various methods have been evolved of making the adsorption measurable. Thus Bachmann and Brieger (156) have measured the heat of adsorption of oils on metal dust; in America there has been developed an adheroscope in order to study the quantities of adsorbed oil ~~gravimetrically.~~ Kadmer ~~(157) nevertheless~~ states in his new work that he has not been able to establish any connection between the dipole moment and the lubricating capacity.

According to the results now available to us with phosphorus compounds, we require of the molecule of the additive that, in addition to the P-atom, it should contain a further particularly active group, by means of which it attaches itself to the sliding surfaces. Otherwise the action of such trifling quantities as 0.1% would be impossible to explain. I do not, however, consider that this adsorption is the decisive factor in the whole process. This is rather the reaction with the surface. Hence the occasionally entirely different behaviour when the materials are altered, and therefore also the highly polished surfaces after running (see Figs. 21 and 22), as have also been ascertained in experiments by Messrs. Daimler-Benz. With very aggressive materials (phosphenyl chloride), the attack on the surface of the metal, probably through the hydrochloric acid produced, was nevertheless so violent, although it is remarkable that this compound has no improving action with silver bearings (AgCl !) Other materials nevertheless have the power of smoothing or removing those points and jags which are still exhibited even by finely treated surfaces. This prevents tearing the film of lubricant and therefore the seizing of the metal parts. It is interesting in this respect that, according to experiments by Prof. Glocker on the electrolytic etching of polished steel sections with phosphoric acid - acetic anhydride, traces of the treatment completely disappear.

In phosphenyl chloride the active group consists of the two chlorine atoms-  in phosphenylous acid  and in diphenyl phosphate  these ~~are the~~ acid ~~OH~~ groups. The phenyl phosphinic diphenyl ester  also contains the configuration



$=\mathrm{P}(=\mathrm{O})\mathrm{OH}$, but here the OH group is etherified with phenol.

It should be noted in this connection that the esterification of the OH group in diphenyl phosphate strongly prejudices the activity. According to our previous experience, to these two molecular parts (P and the active group) must be added at least one aryl or alkyl group, as otherwise the phosphoric acid would have to display great activity  $(HO)_2P(O)OH$ which is not in fact the case. The activity is enhanced by the addition of halogen to the nucleus. The P position was first of all selected, because p-halogen phenols are easy to manufacture. Furthermore, Lincoln, Byrkit and Steiner (158), with the aid of the Timken machine, have ascertained in the case of simple aromatics, that as a rule those compounds with the halogen in the p-position, exert a greater influence on the strength of the film. More recent preparations, having the halogen in the o-oposition, would afford a possibility of comparison. To what cause the improvement in activity through the inactive nuclear halogen can be attributed, cannot be stated with certainty. It is quite possible that in the extreme conditions in which it paves the way for a further improvement, the halogen also takes part in the reaction with the sliding surfaces. Fluorine, chlorine and bromine were found to be of equal value in these experiments. It was first of all considered that the acidity played a decisive part in the occurrences on the surface and that the halogen helped the diphenyl phosphate to acquire an optimum value. It is well known that chlorophenol is more strongly acid than phenol. Exact measurements of the p h value do not, however, support this view. The results of the measurements will be briefly mentioned. They were carried out with a quinhydrone electrode.

Substance	Concentration	ph Value Measured with The Quinhydrone Electrode	ph Value Measured with the Foil Calorimeter
Diphenylphosphate	10^{-4} Mol/l	2.0	2
Di-p-chlorphenylphosphate	10^{-4} Mol/l	1.9	2
Di-p-nitrophenylphosphate	10^{-4} Mol/l	2.0	2
Diphenylphosphate	0.1 wt.%	2.7	2.7
Di-p-chlorphenylphosphate	0.1 wt.%.	2.4	2.5
Di-p-nitrophenylphosphate	0.1 wt.%	2.4	2.5

Some support for the view that the halogen only acts under extreme conditions is afforded by the behaviour of the phenyl phosphinic acid p-chlorphenyl ester. The halogen free ester attains of itself, such extremely high values (over 900 kg/sq cm) that the halogenated ester does not therefore show any improvement.

Since no progress was achieved by ascertaining the acidity, other experiments were initiated, in order to shed further light on the processes on the surface of the metal. I should like to preface my remarks by saying that in accordance with modern opinion, with a coefficient of friction of 0.01-0.1, as was normally the case on the Siebel-Kehl apparatus, we were in the zone of partial lubrication (mixed friction). Although this lubricating condition is probably to be found in many technical bearings (running in), it has been avoided by writers who have recently occupied themselves with oil tests. The latter mainly devote themselves to boundary lubrication, as in machines where partial lubrication prevails, the lubricating ability cannot be evaluated. Boundary lubrication is more easily determined and possibilities of explaining the action of given additives are present to a greater extent. It is however certain that the evaluation of lubricating ability, as demonstrated by the Siebel-Kehl-machine, can be applied qualitatively to technical bearings (see part 4), and this fact was of decisive importance in these experiments. Experiments using our preparations were also made on the four-ball apparatus of Boerlage, and were likewise found to be active, especially where surface-treated balls were used. The friction conditions on the four-ball apparatus to a large extent correspond to boundary friction conditions. The sequence of activity did not, however, altogether tally with thosefrom the Siebel-Kehl machine. Experiments with boundary friction apparatus with miniature friction surfaces have yielded no results. Since an alloy of the phosphorus with the surface of the metal (see Beeck 149) and FP861597 (159)), under the initially mild experimental conditions at the commencement of operation can no doubt be disregarded, while the coefficient of friction is at once reduced, there remains the possibility of adsorption and reaction of the additive. We have endeavoured to bring about a reduction in the concentration of the additives, which were dissolved in benzol, by shaking with iron powder. At an experimental temperature of 20°C, it was not in this way possible to obtain informative results, and a comparison of the speeds of travel of drops of oil on a glass plate, as recommended by Collingridge (155), was useless. We thereupon decided to concentrate the active materials in the surface of a fluid by measuring the surface tension-with negative result. As Prof. Glocker informed me, an adsorption test with the aid of metal discs, whose weight was ascertained and compared after part of the oil had be thrown off by rotation, yielded no figures that could be reproduced. We finally made use of a method, which Shell N.V. de Petrol Matschaapij has developed (160). 5 gr iron powder are mixed with 3 gr oil and 2 ccm benzene, and 200 ccm of 10% sulphuric acid are poured into a glass filter funnel, placed on a suction flask. Through the bottle flows a stream of carbonic acid, so that no sulphuric acid penetrates the filter. The iron powder mixture is added to the sulphuric acid and left to react for 10 minutes, when the stream of carbonic acid is turned off and the fluid is drawn into the bottle. By titrating with n/10 $KMnO_4$ the quantity of dissolved iron is determined and some indication is obtained as to the moistening ability. If a denotes the quantity of iron that has passed into solution in the blank experiment, b the quantity dissolved in 10 ccm filtrate in the oil experiment, g the grammes of oil weighed out and z the wetting ability, we have:

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

In our measurements we obtained the following values for z:

Rotring pure	2.0 ± 0.2
Rotring + 1 % Triphenylphosphate	7.6
Rotring + 1.2 % Phenylphosphinic acid diphenylester	8.2
Rotring + 1.0 % Phenylphosphinous acid diphenylester	13.8
Rotring + 1 % Di-p-chlorphenylphosphate	26.1
Rotring + 1 % 391 IG	29.0

This shows, therefore, that the particularly active di-p-chlorophenyl phosphate, which from the outset gives a low coefficient of friction, adheres very well to the surface. The relatively slight wetting ability of the phenyl phosphinic acid diphenylester indicates, that the adsorption is not the deciding factor in the effect on lubrication. Thus on the basis of the above results, we come to the conclusion which has already been mentioned: adsorption of the active substances takes place relatively quickly on the surface of the metal. The arrangement in such "epilamial" layers may no doubt be observed in various ways with the aid of X-rays and electrons. With increasing load, the reaction with the surface comes to the fore. The unevennesses are the first to be removed as being the points of heaviest load, and therefore of greatest heating and reaction speed, and they likewise represent the greatest density of additive. Additive, reaction products and molecules of lubricating oil then form a very stable film on the highly polished surface. The formation of a coating on the surface could be observed with the naked eye, even with the highly agressive p hosphenyl chloride, but the formation of definite compounds could not yet be detected. That phosphorus-containing reaction products would have a favourable effect on friction might have been foreseen from the results of the many experiments with the phosphating of metals. In part 4 figures will be found showing that when phosphatised balls are used in the four-ball apparatus, the situation as regards the seizing and welding points is improved. (s. Fig. 5a).

The substances employed by us will be compared with each other below as regards their composition and activity. With this in view, their formulae of constitution were collated. A + signifies good, the letter O medium, and the sign - a non-increased load capacity. With the additives selected by us, the coefficients of friction are on similar lines (but not in the case of sulphur, for example). Exact results are collated in Part 4.

It is striking that the entirely symmetrical substances, such as 28 and 33 do not exert any influence on the lubricating properties, although they contain trivalent phosphorus. 30 also belongs to this group; besides an aryl group, it has two alkyl groups. They obviously lack the possibility of coming in closer contact with the surface and concentrating there. If, with increased pressure, a very thin film of oil forms, the very small portion of the additive is not sufficient to become active. The neutral phosphoric esters 44, 49, 48 and 50, also 16,17,18, behave similarly. Neither the introduction of halogen in the nucleus nor the replacement of the oxygen atom by sulphur could bring about any improvement. Moreover, the apparent success at first achieved by exchanging an aryl group for an alkyl group (16,17,18) was found to be deceptive. No impurities due to monochloride could conjure up any activity. After experience with 30, the behaviour of the neutral aryl-alkyl phosphates is not to be wondered at. On the other hand, the activity of the series 1=4,3,5, 25,26,27 is at first sight astonishing, as of course 1 only differs from 44 by the absence of an oxygen atom and 27 from 44 by the absence of two oxygen atoms. Nevertheless, their behaviour is quite different in lubrication. An explanation of this is probably to be found in the greater adsorption of 1 and 27 and in their greater ability to react. Owing to the immediate vicinity of the phenyl group and the phosphorus atom, the molecule is able to attach itself to the metal or to react with it. The fact that the P=O - oxygen hinders this is shown from the outset by the lower coefficient of friction of 27 compared with 1. Generally speaking this series exhibits a higher coefficient of friction than the phosphoric ester series, and this may be attributed to the missing OH group. The introduction of alkyl groups into the nucleus (25,26) does not exert any great influence on activity, but facilitates the solubility in the oil, as the solubility of the preparations rises considerably.

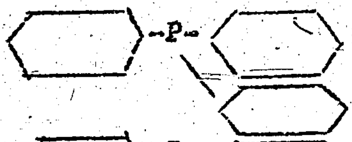
7 and 9 are very active preparations. Improvement by means of the halogen in 9 has already been mentioned. These substances have an acid OH group, by means of which adherence to the metal takes place. The fact that the phenyl group, however, is necessary for bonding of the oil, is shown by the lack of activity of 43. The introduction of halogen in lieu of the hydroxyl group (45,14) increases the resistance to temperature and lowers the activity by a trifling amount. If the oxygen is replaced by sulphur (23, 24, 20,21), the activity is certainly somewhat lessened. The sulphur in combination is not, therefore, active in these compounds, neither is it, apparently, active at high pressures. Elementary sulphur (42) in given concentrations (0.008%) gives medium loads on the Siebel-Kehl apparatus, but has from the outset a higher coefficient of friction. Its action only starts when the metal surfaces are on the point of seizing and is therefore not very suitable as a running-in substance.

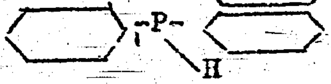
The oxygen bridges in 7 and 9 between phenyl and phosphorus are without significance for the activity, as 38 (I.G. preparation 891) which does not contain them, is very active. Thermally, it is relatively stable. It was preceded by 36, also possessing excellent activity, but liable to decompose at 250°. In 36 and 38 or 37, the OH groups may be replaced by halogen, without the activity being very much changed (2,32). In 31, the chlorine atoms are finally replaced by hydrogen. This very active preparation cannot, however, be used owing to other properties. The fact that the hydrogen atoms also favour adherence to the metal is remarkable, but a partial oxidation of this preparation by the atmosphere cannot be excluded.

It should be mentioned that the insertion of N between aryl and phosphorus annulled the activity (40,41).

In considering the structure of the corresponding combinations we therefore have the likelihood of the primary effect of adsorption The type of products formed by the secondary effect, the reaction with the surface, has not so far been ascertained.

In the course of our work we have synthesised a large number of phosphorous compounds in part hitherto unknown. So far, the activity of some of these materials, in regard to their improving effect on lubricants, has been demonstrated on testing apparatus, bearing test rings and in engines. Application to the engine naturally makes extremely severe demands on the preparations. Further tests, including tests in gears, are in process. It can be taken as a fact that the introduction of halogen in the p-position into the nucleus of aryl esters of phosphoric acid increases activity, while the introduction of an alkyl residue improves solubility in mineral oils.

28  -

29  -

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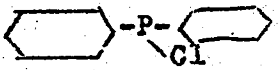
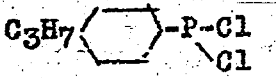
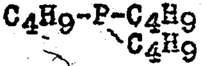
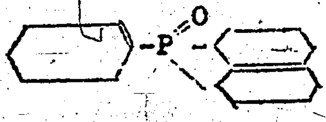
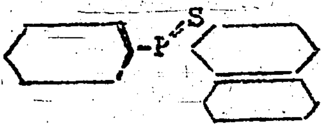
32  +

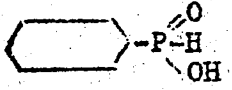
6  +

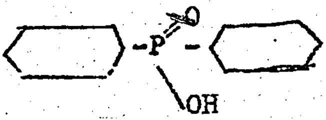
33  -

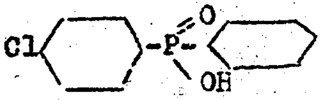
$C_4H_9-P(C_4H_9)-C_4H_9$

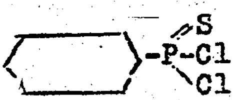
34  -

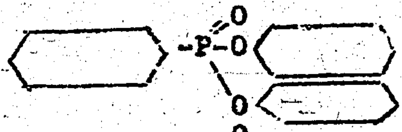
35  -

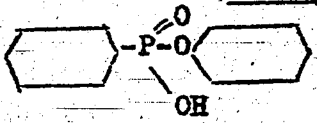
36  -

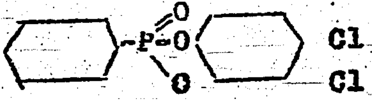
37  ?

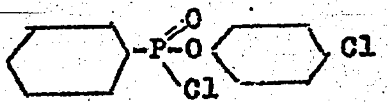
38  +

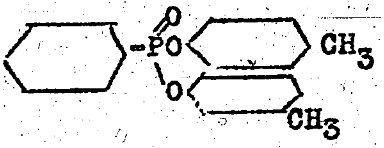
39 

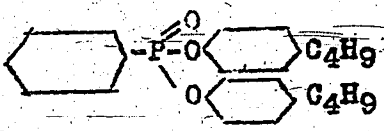
1  +

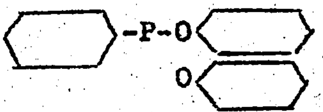
4  σ

3  σ

5  +

25  +

26  +

27  +

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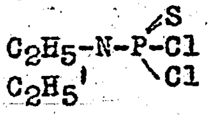
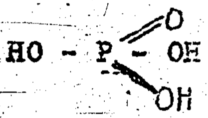
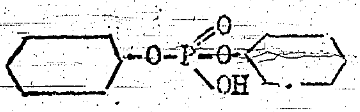
41  -

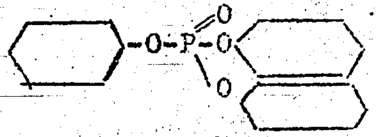
$(C_2H_5)_2N-P(=S)Cl_2$

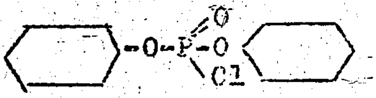
42 S σ

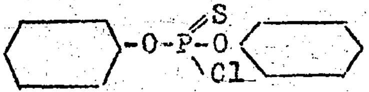
43  -

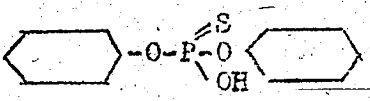
$HO-P(=O)(OH)-OH$

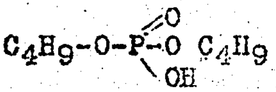
7  +

44  +

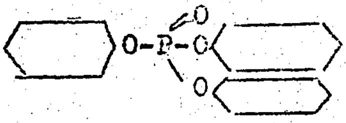
45  +

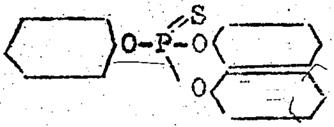
25  σ

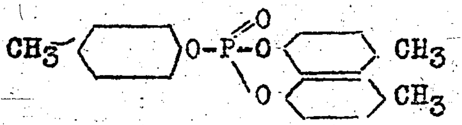
20  +

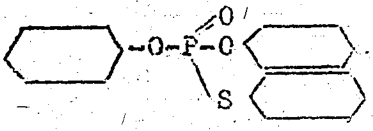
46  σ

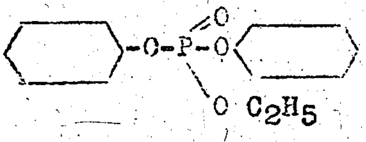
$C_4H_9-O-P(=O)(OH)-O\ C_4H_9$

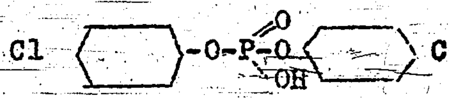
47  -

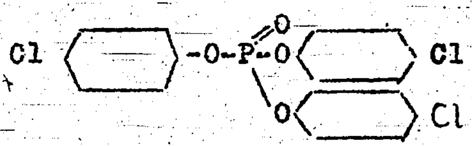
48  -

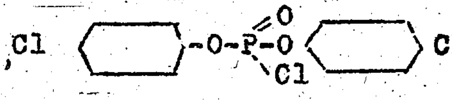
49  -

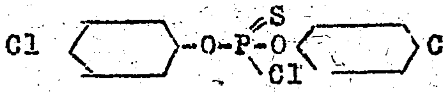
22  -

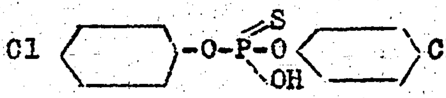
15  σ

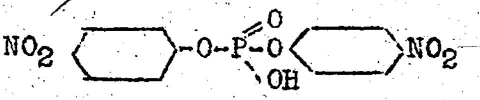
9  +

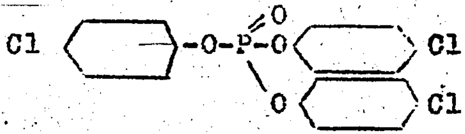
50  +

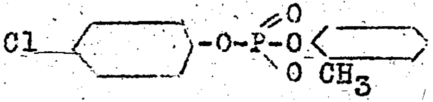
14  +

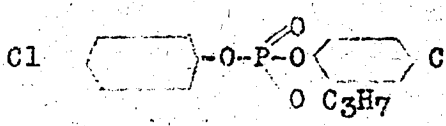
24  σ

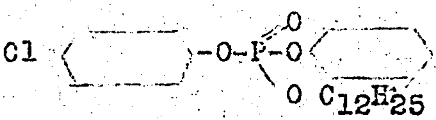
21  +

8  σ

51  -

16  σ

17  -

18  -

2. Making the Preparations

1. Phenylphosphic acid diphenyl ester
2. Phosphenylchloride
3. Phenylphosphic acid di-p chlorphenyl ester
4. Phenylphosphinic acid monophenyl ester
5. Phenylphosphinic acid mono-p-chlorphenyl ester monochloride
6. Isopropylbenzene dichlorphosphine
7. Di-phenylphosphate
8. Di-p-nitrophenylphosphate
9. Di-p-chlorphenylphosphate
10. Di-p-bromphenyl phosphate
11. Di-p- fluorphenylphosphate
12. Di-2,4-dichlorphenylphosphate
13. Dicresylphosphate
14. Di-p-chlorphenyl phosphoric acid monochloride
15. Diphenylphosphoric acid ethylester
16. Di-p-chlorphenylphosphoric acid methylester
17. Di-p-chlorphenylphosphoric acid propylester
18. Di-p-chlorphenylphosphoric acid laurylester
19. Phosphorsulfochloride
20. Diphenyl thiophosphate
21. Di-p- chlorphenyl thiophosphate
22. Diphenylphosphoric acid thiophenyl ester
23. Diphenylthiophosphoric acid monochloride
24. Di-p-chlorphenylthiophosphoric acid monochloride
25. Phenylphosphinic acid dicresyl ester
26. Phenylphosphinic acid di-p-butylphenyl ester
27. Phenylphosphinous acid diphenyl ester.

Substances prepared for the first time

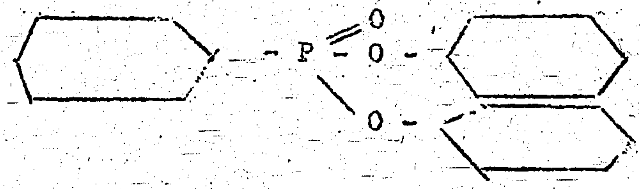
No.	Name	
3	Phenylphosphinic acid di-p-chlorphenyl ester	M.Pt(corr.) 67.5-69.5° pure B.Pt.$_{13}$ 276-277°
5	Phenylphosphinic acid mono-p-chlorphenyl ester monochloride	B.Pt.$_{760}$ 320-435° not isolated
10	p-Bromphenyl phosphoric acid dichloride	B.Pt.$_{20}$ 155-170° ~~not~~ purified
10	Di-p-bromphenyl phosphoric acid monochloride	B.Pt.$_{20}$ 260-280° not purified
11	p-Fluorphenyl phosphoric acid dichloride	B.Pt.$_{15}$ 134-145° not purified
11	Di-p-fluorphenyl phosphoric acid monochloride	B.Pt.$_{15}$ 180-210° not purified
11	Tri-p-fluorphenylphosphate	B.Pt.$_{34}$ 210-213° pure B.Pt.$_{16}$ 235-250° not purified
11	Di-p-fluorphenylphosphate	M.Pt.(corr.) 95-96° pure
12	Di-2,4-dichlorphenylphosphate	--- not purified
16	Di-p-chlorphenyl phosphoric acid methylester	M. Pt.(corr.)131-132° pure
17	Di-p-chlorphenylphosphoric acid propylester	M. Pt.(corr.) 113.5-114.5° pure
18	Di-p-chlorphenylphosphoric acid laurylester	M.Pt. 95 - 100°
21	Di-p-chlorphenyl thiophosphate	---
22	Diphenylphosphoric acid thiophenylester	B.Pt$_{28}$ 288-290°
25	Phenylphosphinic acid dicresylester	B.Pt.$_{26}$ 255-278° not purified
26	Phenylphosphinic acid di-p-butylphenylester	B.Pt$_{20}$ 305-318° not purified
27	Phenylphosphinous acid diphenylester	B.Pt$_{15}$ 225-228° pure

Constants of known Substances recently ascertained

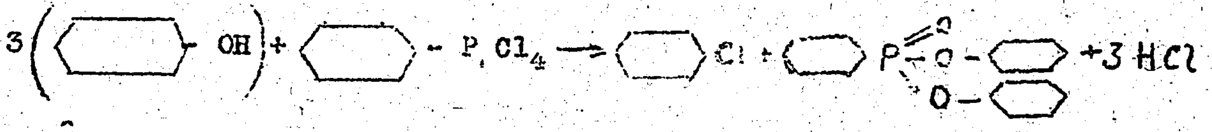
Phenylphosphinic acid diphenylester	M.Pt(corr.) 73-74°	Michaelis[1,2]	MPt 63.5°
Di-p-chlorphenyl-phosphate	M.Pt(corr.) 130-131°	Authenrieth[20] Zetzsche[37]	MPt 126-127° MPt 133-135°
Tri-p-bromphenyl-phosphate	BP_{20} 320-355°	--	
Di-p-bromphenyl-phosphate	M.Pt(corr.) 163.5°	Zetzsche[37]	MPt 199-201°
Di-p-chlorphenyl-phosphoric acid mono-chloride	M.Pt(corr.) 53-54° BP_{15} 225-226°	--	
Tri-p-chlorphenyl-phosphate	M.Pt(corr.) 112-113° BP_{18} 292-295°	Authenrieth[20] Agfa[21]	MPt 99-100° Mpt 112°

1. Phenyl phosphinic diphenyl ester

Beilstein 16/804



Michaelis and Kammerer (1,2) were the first to make this ester. They caused phenol and phosphenyl tetrachloride to act on each other. The result was a thick, oily fluid, boiling at over 360° and solidifying on cooling. While this substance dissolved readily in benzene, ether and ethanol, white needles of M.Pt. 63.5° could be obtained from aqueous alcohol. Aqueous caustic soda had no effect on the ester, while alcoholic caustic soda split it into phenol and phosphenylic acid. This synthesis proceeded in accordance with the equation;



We also started with phosphenyl chloride in making this substance. Into 500 gr. of this we passed, cooling with iced water, a strong, dry current of chlorine, until the whole mass had solidified to form tetrachloride (3). This took 2-3 hours. After adding 1 kg. phenol, when abundant hydrochloric acid was produced, the liquefied mass was stirred vigorously for a time until the generation of hydrogen chloride had abated. Next, distillation was carried out with the help of a salt bath. To begin with, the thermometer rose steadily and a mixture of phenol and chlor-benzene was distilled off. On further distillation at normal pressure, the ester acquired a light yellow colour at 370-380°. Later residues were distilled in vacuo and the BP_{20} 260-270° ester was obtained almost colourless. The yield fluctuated between 95 and 100% (calculated in terms of phosphenyl chloride). The solidified product began to melt at 64.5° (corr.). The melted mass did not, however, become clear until the temperature of 69-73° was reached, according to the starting material. After repeated recrystallisation out of ethanol the melting point was 73-74 (corr.).

16.7 mg. substance (treated in vacuum); 42.5 mg. CO_2, 7.4 mg H_2O

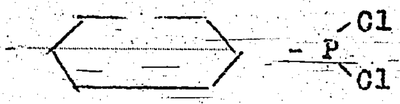
C18H15PO3 (310)	Calculated	C 69.7 H 4.8
	Found	C 69.4 H 5.0

When large amounts were distilled, the ester was no longer distilled, as the light brown product was adequate for our purposes.

In order to test the liability of the ester to be decomposed by boiling water, 20 gr. were boiled for 2 hours with an excess of water. The original product was regained unchanged after completion. We made use of the preparation of large quantities of the ester to test the reaction. From an original amount of 500 gr. phosphenyl chloride and 1000 gr. phenol, the ester was collected after distilling the first runnings of 181.5°C: the yield was 374 gr. On rectification, it boiled between 137 and 181.5°. Already preliminary experiments - distillation of mixed chlor-benzene and phenol - had shown that the two compounds form mixtures with a common boiling point, and these cannot be separated by fractionating. The phenol content was therefore determined analytically. It amounted to 19.78%. The residue of 246 gr. must therefore be chlorbenzene. By treatment with the calculated amount of NaOH (25.9 gr.) in a little water, the phenol was eliminated. The remaining liquor boiled at a constant temperature of 133°. The chlorbenzene yield accordingly amounted to 77.1%. A large part of the missing 21.9% probably escaped in the violent generation of hydrochloric acid during the reaction.

2. Phosphenyl chloride.

Beilstein 16/765 (421)



I had previously prepared a quantity of about 4 kg. phosphenyl chloride in accordance with the second Michaelis process (4, 5 and 6), which was improved by Gruettner and Wiernick (7). Meisenheimer (8), who has adopted both methods, states that the aluminium chloride process is far and away the more convenient. In my opinion, however, it has a number of important disadvantages compared with the pyrogenic method of preparation, and these disadvantages impede the preparation of large quantities. Even the supply of sufficiently large quantities of pure aluminium chloride causes great difficulty today, and technical $AlCl_3$ lowers the yield appreciably. The whole of the aluminium chloride and large amounts of benzene and PCl_3 are lost in the process. The disagreeable aluminium chloride sludge involved large-scale purification work. Furthermore, each time vacuum distillation is necessary, which is no easy matter on a laboratory scale in vessels over 4 litres. Finally it has been shown that in contrast to the usual experience, large amounts of the initial substance (1 kg. benzene and PCl_3) furnished very much smaller yields than the residue I obtained from amounts of the starting substances (400 gr.) I selected. Even the use of home-made aluminium chloride, aluminium and mercuric chloride or additions of calcium carbonate, boric acid, phosphorous pentoxide, tin tetrachloride and silicon tetrachloride (9) afforded no improvement in the yield.

It was then that a firm entrusted with working out a method of preparation adopted the course indicated by Bowles and James (10). Here, however, the heating of a quartz apparatus constructed according to their specifications, caused extremely great difficulties. Chrome nickel wire of different thicknesses, even tungsten wire, was found inadequate. Experiments with sillite rods and chrome nickel tape have likewise not yet produced any positive results. For reasons connected with the apparatus, too, this arrangement does not seem a suitable one for making large quantities. Yields of 80 gr. in 24 hours were the most that have so far been obtained.

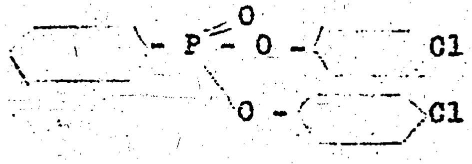
I therefore decided to adopt the first method of Michaelis, the reaction of benzene and phosphorus trichloride in the presence of heat - but in an improved apparatus. While Michaelis only obtained on an average, 100 gr. in 10 hours (11), Pope and Gibson (12) increased the yield by introducing carbon dioxide, to 140 gr. in 9 hours. Arbusow (13), by filling the heating tube with unglazed pieces of earthenware, obtained 11/2 times the yield of Michaelis and Meisenheimer (8) writes of a further increase by using a quartz tube. I was now able to show that it is easily possible to obtain 5-6 times the yield, so that in a fully active operation (24 hours) 1 kg. phosphenyl chloride can be produced.

The essential features of my apparatus were as follows; The tubes were all very wide in order to preclude stoppage as far as possible. (for dimensions, see Fig, 1 - 2). The connections were of rubber, and at points of contact with hot vapours, of waterglass-talc-asbestos. This putty gave good results. Continuous operation was ensured by filling nozzle to the reflux tube. The stream of CO_2 was set for 3 bubbles per second. This quick current should carry the vapours fairly rapidly through the glowing tube. Heating was by gas and was adjusted to a medium red glow. Temperature measurement with an optical pyrometer on the outer wall of the tube showed 800 - 850°C, and a thermocouple measurement during the reaction in the interior of the tube 730 - 750°. The first runnings resulting from the distillation of the reaction product was used, at least in part, for the next reaction.

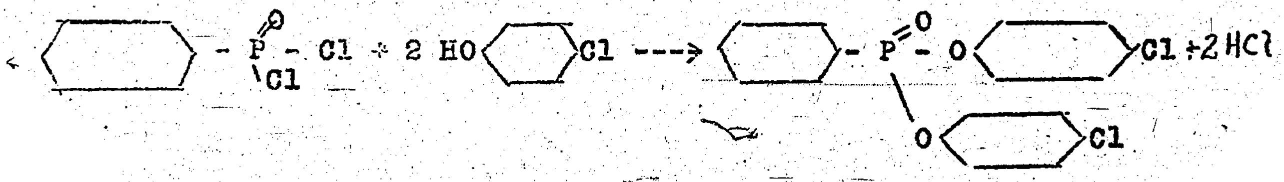
PCl_3 ccm.	C_6H_6 ccm.	First dist. ccm.	Duration hrs	$C_6H_5PCl_2$ yield gr.
500	500	--	6	190
750	750	--	18	330
250	250	1000	25	800
500	500	500	16	850
700	700	100	12	575
600	600	300	14	800
600	600	100	14	900

Experiments with steel tubes also gave serviceable yields.

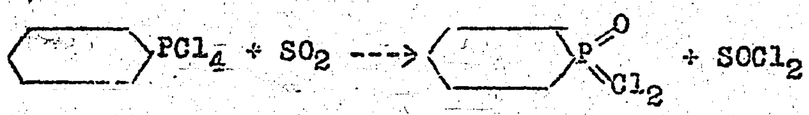
3. Phenyl phosphinic di-chlorphenyl ester



This combination has so far not been described in technical literature. It was prepared in a similar way to its chlorine-free basic substance from chlor-phenol and phenyl phosphinic acid dichloride (1,2).



The dichloride can be prepared from phosphenyl chloride and oxygen (3, 14) or from the tetrachloride with SO_2 (1, 14). We chose the latter method and obtained the dichloride as a thick fluid with BP 257-265 (uncorrected) in a yield of 92% in terms of phosphenyl chloride



In preparing the ester, we used a solvent, 40 gr. chlorphenol 30.5 gr. dichloride and 50 ccm. benzol were heated on the waterbath, nitrogen being passed through and the reflux cooler in position, until no further hydrochloric acid could be detected in the stream of gas. This was the case after 12 hours. The benzol was evaporated and the residue distilled in vacuo. BP_{13} 276-277. The yield was 43 gr., i.e. 74% of the theoretical figure. The thick oil did not at first crystallise, even in the refrigerator at -14°, but solidified spontaneously after a few days. It was treated with hot water to eliminate any chloride adhering to it, shaken up with ammonia and recrystallised from aqueous alcohol.

Chlorination of phenyl phosphinic acid diphenyl ester

An attempt was made to chlorinate the ester direct and thus introdude 3 chlorine atoms. For this purpose, 100 gr. ester were treated at 90-100° with chlorine, some iodine being added. The result was a chlorine absorption of about 8.5 gr. per hour. After 4 hours the weight had increased by 34.5 gr., which must have corresponded to the desired absorption of chlorine.

The product of the reaction was fractionated at a vacuum of 13 mm. The 132 gr. of crude product first of all gave a forerunning (10 gr.) of grease consistency and yellow colour. Then came the main portion at BP_{13} 255-300° in the form of a highly viscous, yellow liquid (85 gr.). The residue was a black, asphalt like mass.

The chlorine determination showed that only 2 atoms of chlorine had attached themselves and probably these were in the phenol nucleus.

30.5 mg. of the substance produced 23.44 mg. AgCl (Carius).

Chlorine ascertained: 18.80%, calculated for 2 atoms chlorine: 19.78%

4. Phenyl phosphinic acid monophenyl ester (3,14).

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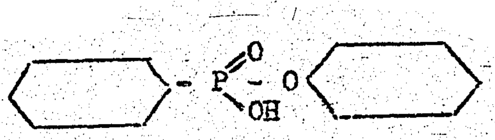
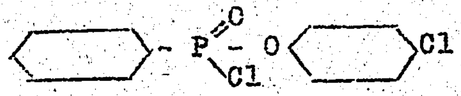


As in the case of Preparation 3, phenyl phosphinic dichloride was first of all made. 27 gr., dichloride were heated with 13 gr. phenol, nitrogen being passed through, in the reflux, until no further hydrogen chloride was generated. It was then fractionated. First of all came slight first runnings, then the main quantity at 320-380°. The distillate was boiled with water in order to saponify the chloride and the residue solidifying after cooling at 50° was treated with concentrated ammonia water. The residual diphenyl ester (9 gr.) was filtered off and the monophenyl ester precipitated with hydrochloric acid. For purposes of complete separation, we allowed it to stand overnight.

In an experiment to restrain the formation of the diphenyl ester, we started out with sodium phenolate and treated it with the dichloride, as above. Here again a large quantity of neutral ester was obtained.

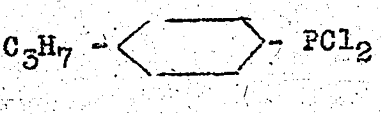
5. Phenyl phosphinic mono-p-chlorophenylester monochloride.



Here again, as in Preparation 4, the neutral ester formed at the same time could not be separated by distillation; the separation method with ammonia could not be used in this case, so we took steps to restrain the formation of the neutral ester to a great extent. We succeeded in doing so by completing the reaction in the shortest possible time. 20 gr. phenyl phosphinic acid dichloride were heated with 14 gr. chlorphenol for 2 hours under reflux and immediately distilled. After first runnings of 300-320° (1 gr.), the main fraction of 320-435° (18 gr.) was collected. There were slight after runnings of 435-440°. In the distillation flask there was also a small quantity of a black residue.

In order to determine the monochloride content, part of the distillate was brought to the boil with n/10 NaOH for ½ hour and the excess lye was back titrated. With a weighed out amount of 1.7567 gr. distillate. 104.15 ccm n/10 naOH were used. The monochloride content accordingly amounts to 87.3% of the main fraction, i.e. 56.5% yield calculated from the starting material. In calculating the amount of soda lye consumed, it should be remembered that for 1 mol chloride, 2 mols of lye are used. In blank experiments, neutral ester was heated with soda lye, but n/10 NaOH was not used up.

6. Isopropylbenzenedichlorophosphine (15)

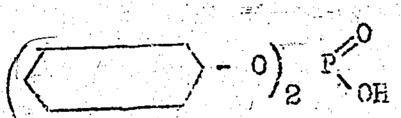


Into 250 gr. isopropylbenzene and 10 gr. anhydrous aluminium chloride, 290 gr. phosphorus trichloride were dropped and the whole stirred.

Heat was then applied for 48 hours in the sandbath under reflux. During this period, a further 15 gr. aluminium chloride were added in 2 portions, when the generation of hydrogen chloride had become very weak. Stirring was continued throughout the day (altogether 20 hours). On the completion of the reaction, first the unchanged phosphorus trichloride was distilled off under normal pressure, then the isopropyl benzene under reduced pressure. The residue consisted of a red fluid and a light crust. The liquid was poured off and fractionated at 10 mm. The first runnings were small and then 75 gr. of a colourless liquid, boiling at 125-127° were obtained. The yield was thus 16% of the theoretical figure, in terms of isopropylbenzene. The isopropylbenzene-dichlorophosphine was again fractionated in a vacuum. The viscous residue likewise contains considorable quantities of the phosphine. In order to avoid wastage, it is however more practical not to treat it, but to use it in the next operation as a catalyst, in place of aluminium chloride.

7. Diphenyl phosphate

Beilstein 6/178 (95)



The phosphoric esters of the aliphatic and aromatic oxy-substances have acquired increasing importance during the last 20 years. The neutral phenol esters of the most varied phenols are used on a large scale as softening agents, insulating material, wetting agents, lubricants and for purifying waste gas and water. There are also a large number of minor applications. As I started out with neutral esters for preparing my disubstituted esters, I should like to give a brief account of their manufacture. Triphenyl phosphate was first made by Jacobesen (16), later by Heim (17) from phenol and phosphorus oxychloride by heating and then fractionating. The by-products thus obtained comprise phenyl phosphoric acid dichloride (BP$_{11}$ 121 (18)) and diphenyl phosphoric acid monochloride BP$_{13}$ 195 (18)). The neutral phenol ester melts at 49° (19) and has a BP$_{11}$ of 245°. Authenrieth prepared it by acting on an alkaline solution of phenol with phosphorus oxychloride at a low temperature (20). The Agfa then avoided the generation of large quantities of by-products and the troublesome production of hydrogen chloride by decomposing $POCl_3$ with sodium phenolate (21). A simplification of Jacobsen's reaction was obtained by the Imperial Chemical Industries Ltd (22,23) by the addition of basic substances such as aniline, pyridin, toluidin, see also Fischer (24), while Adickes, Brunnert and Luecker (25) and the Dow Chemical Co. (26) used $SnCl_4$, $AlCl_3$, $MgCl_2$ as catalysts with excellent results. As a substitute for phosphorus oxychloride, the Celluloid Corporation (27) use PCl_5 and water, the Victor Chemical Works (28) pentachloride and pentoxide. Methods of less significance are the reaction of diaryl sulphite with PCl_5 by Carre and Libermann (29) and the oxidation of triphenyl phosphite by means of air, SO_3, nitric oxides and the corresponding catalysts, such as vanadium pentoxide (30,31).

Diphenyl phosphate is obtained at once, according to Authenrieth, by the above process (20) by the mere action of the alkaline phenol solution with $POCl_3$. The formation of this ester has been described by Rembold (32), from P_2O_5, and its production by saponifying triphenyl phosphate with strong alkali by Glutz (33), Jacobsen (16), Rapp (34), Hoeflake (19), also Brigl and Müller (35) saponified the monochloride by water or dilute alkaline solution.

As we had technical triphenyl phosphate at our disposal, we first of all used this and treated 1 mol neutral phosphate, which was suspended in water, with 2 mols NaOH. On heating until the water boiled and by using large quantities, an extremely violent reaction was brought about. The clear solution was next acidified with hydrochloric acid. The typical odour of phenol was then ascertained. It was then mixed with excess of soda and the phenol was eliminated (the phenol not transformed into sodium salt) by ether extraction (6 times). To begin with, a large amount of ether dissolved in the alkaline liquid; the ether was eliminated from the water-bath and allowed to cool. On acidifying, the diphenyl phosphate was at once precipitated in fine, white crystals. It was filtered off and dried in the air. The yield was quantatative. Experiments to eliminate the phenol with steam did not produce good results. The greatest quantity treated by us in the manner described above amounted to 2 kg. triphenyl phosphate.

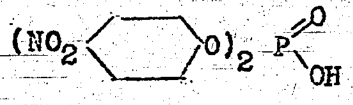
In a process for preparation after Authenrieth (20), 87 gr. triphenyl and 14 gr. diphenyl phosphate were obtained from 94 gr. phenol and 52 gr. $POCl_3$.

A further experiment aimed at saponifying the monochloride. 306 gr. $POCl_3$ and 376 gr. phenol yielded, after heating for 20 hours, 50 gr. dichloride and 255 gr. monochloride. On warming with dilute alkali, the latter produced plain diphenyl phosphoric acid.

The ester precipitated by hydrochloric acid is not a homogeneous product. The melting points of the preparations thus obtained vary very much and there are also great differences in solubility. Thus with air-dried substances melting points of 66-68°, 67-69°, 48-110°, and 49-115° were obtained. Under certain experimental conditions, a dehydrated product is thus obtained direct (MPt 70° Hoeflake (19)), while in other cases a mixed preparation was the result. However, all these preparations, on contact with the air, pass in the course of a few days either into the diphenyl phosphate continaing 2 H_2O of MP (corr.) 50-51°, or into the anhydrous product of MP (corr.) 68-69.5°. The hydrated preparation is always obtained in fine crystals when recrystallised from boiling water, but one portion always remains in solution and must be precipitated with acid. After remaining in the vacuum desiccator, anhydrous diphenyl phosphate is always produced. The intermediate product with a higher melting point, which is responsible for the long intervals in melting, and imparts to the whole preparation an abnormally poor solubility in oil, was not investigated further; possibly it is a pyrophosphate. All these facts account for the contradictory references in technical literature. Rapp (34) indicates MP 56°, Authenrieth (20) 61-62°, Hoeflake 51° and 70° as the true figures. In order to test whether the diphenyl phosphate is not capable of distillation, the substance was slowly heated in the oil bath at 0.09 mm Hg: At 210-230° crystals began to separate out in the mixture, but they melted at very much lower temperatures than 45°. The ester had therefore already decomposed and phenol was distilled off.

8. Di-p-nitrophenyl phosphate

Beilstein 6/237



In order to prepare it, I first attempted to start with triphenyl phosphate, which was nitrated and then saponified, but during saponification the molecule was completely split. To 100 gr. 100% nitric acid there were then added, stirring well, at -3 to -5°, 25 gr. finely powdered triphenyl phosphate portion by portion, after which stirring was continued for 3 hours at 20°. The nitrated product was precipitated with water from the homogeneous liquid, extracted and washed in water until free from acid. The yield was 35 gr., i.e. 95% of the theoretical amount. The melting point of the product MPt (corr.) which was recrystallised from iced acetic acid, was 156-157°. Rapp (34) gives 155°. 5 gr. of triphosphate were heated with 0.5 gr. NaOH in an alcoholic solution for 1 hour on the water-bath. It was then treated in the usual way, but only p-nitrophenol could be isolated. Attempts to saponify triphenyl phosphate in the same way were successful, consequently the failure was due to the nature of the tri-p-nitrophenyl phosphate. A preliminary experiment to nitrate triphenyl phosphate with 65% nitric acid yielded only the starting material unchanged. A further experiment dealt with the usual method of heating phenol and phosphorus oxychloride. At first hydrogen chloride was generated as customary, but on further heating, charring occurred and the mass swelled up. Rapp also found this (34) as we observed later, but it is possible that this reaction might be carried out all the same by keeping the temperature down.

Shaking up p-nitrophenol in alkaline solution with phosphorus oxychloride after Authenrieth (20) likewise failed to produce a result.

When diphenyl phosphate was nitrated with 100% nitric acid, only p-nitrophenol was obtained. Rapp's method (34), however, only furnishes very trifling yields.

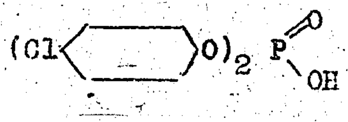
Finally, the preparation was obtained in a good yield after Hoeflake (19). 10 gr. diphenyl phosphate were added at -5 to -10° to 30 ccm HNO_3 (s.g. 1.49), and stirred; the liquid obtained was at once decanted into water. An oil was separated out which solidified overnight in the refrigerator. It was rinsed with conc. hydrochloric acid. To free the product from isomers, it was recrystallised twice from ethyl acetate. MP (corr.) 174.5 - 175.5°. The crude product normally contains 15-16% θ-nitrophenol

30.8 mg. substance give 2.12 ccm N_2 at 21° and 750 mm Hg.
22.30 mg. " " 1.65 " " " 26° " 744 mm Hg.
found 7.8% nitrogen, calculated 8.2%
found 8.2% " " 8.2%

The preparation dried in the vacuum desiccator absorbs 1 mol water in the air.

9. Di-p-chlorophenyl phosphate.

Beilstein 6/188 (?)



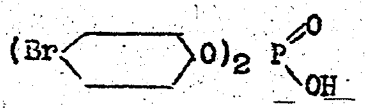
This ester can also be obtained conveniently in various ways. We prepared it once by saponifying monochloride and another time by treating triphosphate with aqueous caustic soda. By combining the two methods the production of large amounts for laboratory work could be very much simplified.

The triphosphate was obtained by Authenrieth (20) from chlorophenol and phosphorus oxychloride in an alkaline solution, and a melting point of 99-100° was obtained. The Agfa Co. prepared the ester from sodium phenolate and $POCl_3$ (21) and give a melting point of 112° for it. Durrans (36) obtained the product from triphenyl phosphate and sulphuryl chloride, using iron powder as the catalyst. For the complete elimination of the iron, the latter method requires the distillation of the whole substance and was not, therefore, considered. Di-p-chlorophenyl phosphate was also first obtained by Authenrieth (20) as a secondary product in the preparation of the triphosphate. He also made it by saponifying the triphosphate with alcoholic potash and obtained from dilute hydrochloric acid plates of melting point 126-127°. Zetzsche and Nachmann (37) obtained for their preparation (obtained by saponification from monochloride and neutral phosphate) a melting point of 133-135° (corr.).

The original material - p-chlorphenol - was obtained by ourselves in accordance with Dubois' method (38,39) by the action of excess sulphuryl chloride on phenol, separating the isomers by fractional distillation. From 2 kg. phenol and 3.2 kg. sulphuryl chloride, mixed drop by drop within the space of 6 hours, we obtained 624 gr. of 185-200° and 1900 gr. of 200-217°. The higher boiling chlorphenol was purified by freezing and centrifuging. Into 3 mols p-chlorphenol (385.5 gr.) there are allowed to drop 1 mol $POCl_3$ (153.5 gr. + 30 gr. excess owing to losses, as HCl accounts for some), stirring well, and the whole is then heated until the generation of HCl is over at the reflux. The reaction is completed in about 7 hours. The whole reaction mass is then boiled with aqueous caustic soda until it dissolves in water. The triphosphate will be converted into diphosphate and the dichloride into monophosphate (40). On acidifying, impure di-p-chlorophenyl phosphate is precipitated as oil with chlorophenol. Purification with soda, as with diphenyl phosphate, is not possible here, as chlorphenol forms a sodium salt as well. The Chlorophenol was therefore to a great extent eliminated by steam distillation, a method which does not seem very suitable for large quantities. The crude diphosphate yield was about 225 gr, i.e. 70.5% of the theoretical amount (the whole reaction is calculated in terms of triphosphate). On recrystallising from benzene, the residual phenol remains in solution. Recrystallising was finally also undertaken from water. The di-p-chlorophenyl phosphate was precipitated in shining crystal flakes and had a melting point (corr.) of 130-131°.

In preparing diphosphate from pure monochloride, we allowed the latter to drop into 2n NaOH at 70-80°, stirring well. After a little time, further water had to be added to complete solution. We secured from 630 gr. monochloride, 570 gr. diphosphate, i.e. 95.5% of the theoretical amount. This method is preferable because troublesome purifying processes are not required.

10. Di-p-bromophenyl phosphate



Of the p-bromophenyl phosphoric esters, there have so far been obtained; tri-p-bromophenyl phosphate by Authenrieth and Mühlinghaus (41). They decomposed phenyl acetate with PBr_5 and obtained a small quantity of the ester with a melting point of 101°. Glutz (33) obtained the same substance from triphenyl phosphate and bromine in the sealed tube. Zetzsche and Nachmann (37) obtained the di-p-bromophenyl phosphate from diphenyl phosphate and bromine in boiling chloroform and ascertained for the substance which was recrystallised from water or $CHCl_3$ a melting point of 199-201. The monophenyl phosphate, which is of less interest here, is also known (37,42).

As we required a large amount of the substance, we had recourse to more prolific methods of production. We reacted bromophenol with phosphorus oxychloride. The p-bromophenol required was made in accordance with the method of Adams and Marvell (43). Bromine is allowed to act on phenol, cooling and stirring, in carbon disulphide and the isomer mixture is fractionated using a column after eliminating the solvent; we used for this purpose a 3 cm layer of glass Raschig's rings. The boiling point of the p-bromophenol was BP_{25} 145-150°. With an original quantity of 500 gr. phenol, the yield was 750 gr. i.e. 81% of the theoretical amount.

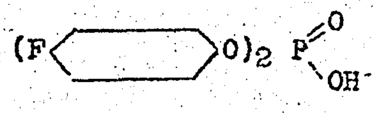
340 gr. p-bromophenol (1 mol) were heated to 190° and 1 mol of phosphorus oxychloride dropped in, stirring well. A violent stream of hydrogen chloride was generated. On completing the dropping process, the mixture was heated for 10 hours under reflux and the reaction product was then fractionated.

120 gr. p-bromophenyl phosphoric acid dichloride BP_{20} 155-170°.
200 gr. di-p- " " " monochloride BP_{2} 260-280°.
105 gr. tri-p- " phosphate BP_{20} 320-335°.

The individual fractions were not further purified. To make the diphosphate, the monochloride or the triphosphate can be saponified. When triphosphate was boiled with aqueous caustic soda, bromophenol was produced. The diphosphate goes into solution as a sodium salt and is separated out again by conc. HCl as a light coloured oil. After being washed with cold water, the oil solidifies to form a colourless crystalline mass. This is recrystallised from hot water. The diphosphate crystallises in shining crystal plates and has a melting point (corr.) of 162-163.5°C.

Diphosphate could also be obtained from di-p-bromophenyl phosphoric acid monochloride, which solidifies at room temperature, by boiling with aqueous caustic soda. Melting point (corr.) 163.5. It is noteworthy that Zetzsche and Nachmann found a very much higher melting point: 199-201° (37).

11. Di-p-fluorophenyl phosphate



$$(F\text{-}C_6H_4\text{-}O)_2P(=O)OH$$

Phosphoric esters of the p-phenol fluoride are not so far known. p-fluorophenol was obtained by Schiemann's borium fluoride method (44) through anisidine. For this purpose, freshly distilled anisidine was diazotised and the diazonium solution was acted on by fluoboric acid. The resultant liquor was extracted and the solid part dried in the vacuum desiccator. Pyrogenic decomposition then followed. The anisol fluoride thus obtained was saponfied with aluminium chloride and a good yield of phenol fluoride of BP_{14} 81-84°.

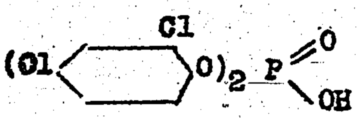
26 gr. p-fluorophenol (2 mols) were heated under reflux with 19.4 gr. $POCl_3$ (1 mol) for 15 hours until the generation of HCl was over, and the reaction product fractionated in vacuo; p-fluorophenyl phosphoric acid dichloride BP_{15} 134-145°.

Di-p-fluorophenyl phosphoric acid monochloride BP_{15} 180-210°.

Tri-p-fluorophenyl phosphate BP_{16} 235-250°.

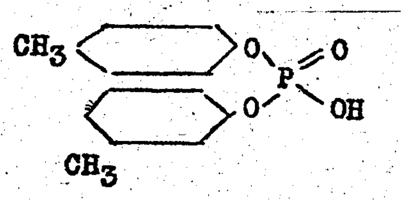
The crude monochloride yield was 18 gr. It was again distilled and had a BP_{34} 210-213°. Treated with aqueous caustic soda and worked up in the usual way, the diphosphate was obtained. By way of contrast to the chlorine and bromine derivative, the fluorine derivative is only produced from water on acidifying. We obtained fine, shining crystal flakes, which on being dried in a vacuum, possessed a melting point MP (corr.) 95-96°. With the C-determination the substance was found to be very difficult to burn and gave too low figures. The triphosphate also solidified at low temperatures.

12. Di-2.4-dichlorophenyl phosphate.



The 2.4-dichlorophenol was prepared free from isomers according to the date of Kohn and Sussmann (45), by passing dilute chlorine over phenol at a low temperature. The product obtained was then treated with the corresponding amount of $POCl_3$. Without fractionating, it was then immediately saponified with soda lye and the diphosphate was isolated as usual. There was first formed a clear syrup, which after a few days crystallised in the refrigerator.

13. Dicresyl phosphate.



This was obtained from technical tricresyl phosphate by heating with NaOH. The dicresyl phosphate was a reddish syrup.

Experiment with dichlororesorcine

Dichlororesorcine was obtained according to Reinhard (46) and heated with $POCl_3$ in the reflux. The result was a resinous, transparent brittle mass, which could not be saponified in the usual way with caustic soda.

14. Di-p-chlorophenyl phosphoric acid monochloride

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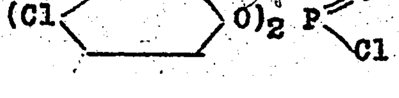


This chloride was obtained by Authenrieth (20) from di-p-chlorophenyl phosphate and PCl_5 by heating and instead of being isolated from the solidified mass, was converted to amide. We made the preparation by treating chlorophenol with phosphorus oxychloride. To do so, 1280 gr. crude p-chlorophenol (Bp 202-218°) were heated with 875 gr. $POCl_3$ for 19 hours under reflux and the reaction product was subjected to fractional vacuum distillation:

430 gr. p-chlorophenyl phosphoric acid dichloride BP_{26} 160-220°.
1030 gr. di-p-chlorophenyl phosphoric acid monochloride BP_{23} 220-270°.
230 gr. tri-p-chlorophenyl phosphate in the residue.

From the 430 gr. dichloride there were obtained by heating with 260 gr. p-chlorphenol a further 327 gr. monochloride and a large amount of triphosphate, while the first runnings amounted only to 35 gr.

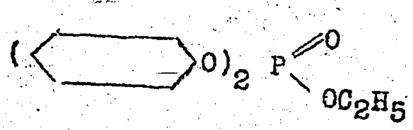
After repeated fractionating, the monochloride had a BP_{15} 225-226°. Analysis after Carius: 200.7 mg substance, 257.0 mg AgCl. $C_{12}H_8O_3Cl_3P$ (337.5), found Chlorine 31.7%, calc. 31.3%

Even after standing for a day at -15°, the oily, colourless liquid did not solidify, but after about 3 weeks spontaneous crystallisation took place. From hexane we obtained colourless and almost odourless crystals of melting point (corr.) 53-54°.

The triphosphate was likewise distilled (BP_{18} 292-295°) and recrystallised from ether; melting point (corr.) 112-113°.

15. Diphenyl phosphoric acid ethyl ester.

Beilstein 6/179



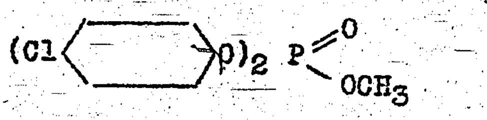
For preparing the mixed esters of this type, the following possibilities presented themselves:

1. Reaction between triphenyl phosphate and sodium alcoholate (Morel 47)
2. Reaction of diphenyl phosphoric acid monochloride and sodium alcoholate (Morel 48)
3. The use of phosphoric acid alkyl ester dichloride and sodium phenolate (Morel 49).
4. Direct esterification of diphenyl phosphoric acid with alcohol, with the corresponding elimination of water, e.g. by CaC_2 in Thielepape apparatus.
5. The use of monochloride and alcohol, with the addition of an agent for removing the HCl, such as pyridin.
6. Reaction of sodium diphenyl phosphate with alkyl halogenide.

Methods 1 and 4 were not found to be prolific in preliminary experiments, and with 6 no reaction at all was obtained. The second method was therefore adopted. The monochloride was made in the space of 14 hours under reflux by Rapp (34), who heated 188 gr. phenol and 188 gr. $POCl_3$ (1 mol + 35 gr. excess, see Ephraim (50)). On fractionating we obtained in addition to 125 gr. monochloride, BP_{25} 215°, 80 gr. dichloride.

The monochloride was reacted upon with the calculated amount of sodium alcoholate in ethanol. The reaction took place with the precipitation of common salt. After filtering, the alcohol was evaporated and fractionated in a vacuum. After short first runnings the ester came over BP_{15} 205-220°.

16. Di-p-chlorophenyl phosphoric acid methyl ester

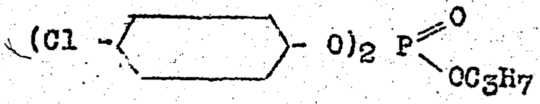


For the preparation of this compound, which was hitherto quite unknown, we also started with monochloride. On treating with sodium methylate, common salt was precipitated. After filtering, it was distilled in a vacuum, and after separating off a copious first running of BP_{28} 240-280, only a small quantity of a solidifying mass was obtained, which had a melting point of 100-105°. An attempt was therefore made to cause the monochloride to react with methanol in pyridine. The reaction product was collected in water. A voluminous precipitate was formed which, when recrystallised from methanol, produced a substance which had not melted at 250°. It was not further investigated.

We next heated 13 gr. monochloride with 1.5 gr. methyl alcohol in ether for 2 hours until it boiled, the ether was then evaporated off and the solidifying residue was recrystallised twice from petroleum ether. The melting point was 131-132° (corr.). The ester dissolves readily in the normal solvents (benzene, ether, alcohol, chloroform). A faintly acid reaction, probably caused by traces of monochloride, was present.

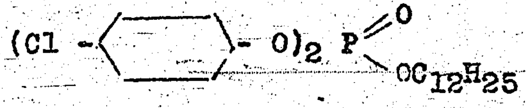
34.34 mg. substance, Carius, 30.22 mg. AgCl, chlorine found 21.7%, calculated 21.3%
17.48 mg. substance, 5.05 mg H_2O, 21.70 mg CO_2
$C_{13}H_{11}O_4Cl_2P$ (333) found H 3.3% C 46.3%
calc. H 3.3% C 46.8%

17. Di-p-chlorphenyl phosphoric acid propylester



Experiments to obtain this ester from the sodium salt of di-p-chlorophenyl phosphate and propyl bromide in absolute alcohol failed completely. Additions of monochloride, sodium and excess propyl alcohol did not produce good results. We therefore took only the exactly calculated quantity of n-propanol, as well as monochloride and sodium, and treated with benzene. 4.6 gr. sodium were caused to react with 11.9 gr. n-propanol and 80 ccm benzene, the whole being heated and hydrogen fed through. After cooling, we allowed 56.8 gr. monochloride in 100 ccm benzene to drop in and heating was continued for a further 3 hours under reflux. It was then shaken up with water and the commonsalt solution was separated in a separating funnel. The benzene layer was dried with sodium sulphate and the benzene was finally evaporated off in a vacuum. The residual oil solidified in the refrigerator and was recrystallised 3 times from petrol ether, until the melting point remained constant. Melting point (corr.) 113.5-114.5°. The substances had a neutral reaction.

18. Di-p-chlorophenyl phosphoric acid lauryl ester



To prepare this substance, 4.6 gr. sodium were covered with 50 ccm dry xylene, and a solution of 37 gr. lauryl alcohol in 100 ccm xylene was slowly dropped in at room temperature. Dry hydrogen was then passed through. It was then heated under reflux at the boiling point of xylene until all the sodium had been converted which occurred after about 5 hours. Cooling with iced water, we then allowed 40 gr. monochloride in xylene to drop into the sodium laurate. The reaction started an addition of heat. The solid laurate was dissolved, but the formation of common salt could not be observed. It was heated for 1 hour up to boiling point, the xylene was evaporated off and the residue collected in ether. The ethereal solution was shaken up with water and with soda solution (to eliminate any di-p-chlorophenyl phosphoric acid present). We next dried with sodium sulphate, evaporated the ether and expelled the remainder of the xylene in vacuo. The residual oil soon solidified. The ester is readily soluble in ether, benzol, glacial acetic acid, chloroform, acetone, ethyl acetate and pyridine, but not so soluble in alcohol and petroleum ether, while it will not dissolve at all in water. The product recrystallised from petroleum ether had a melting point of 95-100°.

19. Phosphorus sulpho-chloride. $PSCl_3$

In order to prepare substances containing sulphur we used a large amount of phosphorus sulpho-chloride. A number of methods have been worked out for preparing it. If we take into consideration the more recent work, where $PSCl_3$ was used as an ancillary substance, a number of methods have been adopted. It was at once apparent that no ideal solution has been found for the laboratory. It was first made by Seruias (51) from sulphuretted hydrogen and phosphorus pentachloride. He was followed by Wöhler and Hiller (52), who caused white phosphorus to act on sulphur monochloride. Both methods were employed on subsequent occasions but, as the materials indicate, they are not exactly pleasant ones. v.Flemming purified the product obtained according to Wöhler by shaking with water (53). Pletz (54) dissolved PCl_5 in CS_2 and passed through pure hydrogen sulphide. Baudrimont caused phosphorus pentachloride to act on antimony trisulphide, but here the elimination of $SbCl_3$ causes difficulties. Simon (55) has also used this method of preparation.

Other writers made use of reactions in closed tubes. Henry (56) heated sulphur and phosphorus trichloride, which at the temperature of boiling PCl_3 do not combine with each other, in a tube to 'about' 130° and obtained a quantitative reaction. When he worked through his experiments again he obtained, despite subsequent raising of the temperature, very different results. In some cases the complete reaction had occurred, in other places the componenets were unchanged or else the reaction was incomplete. By the addition of 1% dry Na_2S as proposed by Woodstock and Adler (57), and by keeping to a temperature of 150-160°, we always obtained quantitative reactions.

Thorpe (58) also melted P_2S_5 with PCl_5 together in the tube and Runo de Fazi (59) worked under the same conditions with P_2S_5 and CCl_4

However, all these methods fail owing to their unpleasantness and loss of time, a feature which is always to be found with experiments in sealed tubes.

More recent technical preparations are based on ferro-phosphorus and sulphur chloride (60). The I.G. has recently evolved a process (61) in which the vapour of PCl_3 is passed over sulphur heated over 140° but not over 160°. I simplified this method for the laboratory by merely dropping the PCl_3 on to the heated sulphur and stirring. The yield corresponds approximately to that obtained by the I.G. with PCl_3 vapour. After a period of reaction lasting 6 hours, the I.G. obtained from 250 gr. sulphur and 500 gr. PCl_3, 205 gr. $PSCl_3$ of Bp 118-122°. We heated 400 gr. sulphur in a 3-neck flask to various temperatures and allowed 250 ccm PCl_3 to drop into it. The sulphur was vigorously stirred, when a KPG stirrer stood us in good stead. The PCl_3-$PSCl_3$ mixture at once distilled at a temperature of 80-115°. It was afterwards fractionated and the residual PCl_3 was re-used. For apparatus see Fig. 3.

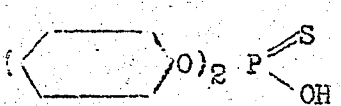
Results of experiments:

No.	Duration of dropping in hrs.	Sulphur temp.	yield	% Th. calc. on PCl_3
1	7	190-200°C	160g	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 (where 4 times the total amount was added	200-210	65	21.1

The series of experiments shows that the temperature used by the I.G. (140-160°) is insufficient if the PCl_3 is added drop by drop. The I.G. states that the temperature selected was particularly favourable because above 160° the sulphur would be too viscous. My experiments, however, showed that the viscosity of the sulphur mass gives no trouble to a glass stirrer up to 250°. We found that, as far as can be stated from our small series, the optimum temperature was 190-210°. Higher temperatures obviously shattered the time of residence of the phosphorus trichloride too much. For laboratory purposes the present method is probably the most convenient.

20. Diphenylthiophosphate

Beilstein 6/181 (96)



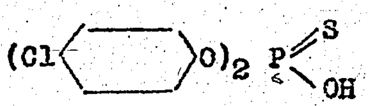
According to Authenrieth and Hildebrand (62), 3 mols phenol (57 gr.)

were dissolved in 120 ccm 20% NaOH and 1 mol $PSCl_3$ was added. The whole was warmed on the waterbath for 2 hours; the oily layer was collected in ether, dried with sodium sulphate and the ether distilled off. The residue solidified in the cold and was recrystallised from alcohol. Melting point (corr.) 53°. The yield was 40 gr.

Sulphur det. after Carius: 37.90 mg substance, 26.72 mg $BaSO_4$, found sulphur 9.7, calculated 9.8%

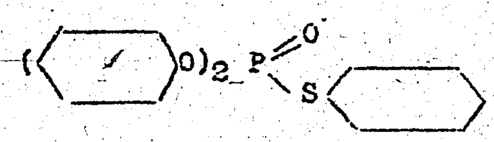
1 mol thiophosphate was heated with 1 mol NaOH (in alcohol, with an aqueous caustic soda, thiophosphate cannot be saponified, according to Authenrieth (68), page 1100) for 2 hours in the water bath, the solution evaporated to dryness; the residue was then dissolved in soda and the phenol eliminated with ether. The aqueous layer was acidified. and again extracted with ether. After drying and evaporating, the ethereal layer left behind a yellowish oil, which could not be distilled in a vacuum without decomposing: diphenyl thiophosphate.

21. Di-p-chlorophenylthiophosphate



The neutral ester was obtained, according to Authenrieth and Hildebrand (62) on quite similar lines to the triphenyl thiophosphate, except that it was not recrystallised, and it was afterwards saponified with NaOH in ethyl alcohol. This produced a dark coloured oil. 64.53 mg substance, 101.31 mg. CO_2, found C 43.8%, calc. C 43.0%. Strecker and Grossmann (65) doubt whether tri-p-chlorophenyl thiosulphate is obtained in this way. Nevertheless, Authenrieth obtained the analogous triphenyl thiophosphate with correct constants in a similar way.

22. Diphenyl phosphoric acid thiophenyl ester



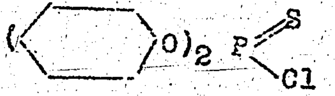
In order to prepare this ester we mixed together calculated amounts of diphenyl phosphoric acid monochloride and thiophenol. At first there was no reaction; this did not commence until pyridine had been added. It was heated for a further 6 hours and the resultant pyridine hydrochloride was dissolved out with water. We then rinsed with dilute hydrochloric acid (pyridine) and then with soda solution, finally with pure water and dried with sodium sulphate. On distilling in a current of CO_2 the following fractions were obtained:

1. First runnings BP_{15} 60-64° (about 10 drops)
2. First runnings BP_{30} 245-275°.
3. Main fraction BP_{23} 275-282°.

On rectifying, the ester was obtained as a colourless oil with BP_{28} 288-290°. The ester was not previously known, although its isomer, triphenyl thiophosphate is a familiar substance.

23. Diphenyl thiophosphoric acid monochloride.

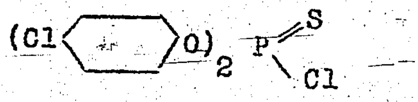
Beilstein 6/181 (96)



The starting material used for this product was phosphorus acid diphenyl ester monochloride. This was ~~obtained~~ by the methods of Noack (63) Anschütz and Emery (64) from phenol and phosphorus trichloride. By the vacuum distillation of the reaction product in a current of CO_2, the chloride was obtained with BP_{11} 172°. The chloride was next heated with the calculated amount of sulphur, according to the process of Anschütz and Emery (18) or that of Strecker and Grossmann (65), for a brief period at 190-200°, CO_2 being passed through at the same time. The reaction product, a brownish mass, was fractionated in vacuo. The product thus obtained with BP_{11} 193-194° was somewhat contaminated by sulphur and therefore yellowish. It was obtained pure by recrystallising from hexane.

24. Di-p-chlorophenyl thiophosphoric acid monochloride

Beilstein 6/188 (107)



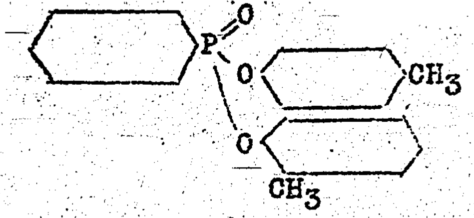
First of all an attempt was made to produce this chloride from sodium-p-chlorophenolate and phosphorus sulphochloride in xylene. All we obtained, however, from 50 gr. $PSCl_3$ and 84 gr. phenolate was 5 gr. of the desired thiochloride. We therefore made it in a similar way to Preparation 23. We first heated 2 mol (238 gr.) p-chlorophenol of BP 210-217°, with 1.5 mol PCl_3 (206 gr.), CO_2 being passed through, for 1½ hours under reflux. It was then at once fractionated:

130 gr. first runnings and dichloride	BP_{12} 0-207°.
135 gr. monochloride	BP_{10} 207-235°.
40 gr. triphosphite	BP_{10} 270°

Preliminary experiments in which, in accordance with recommendations of Strecker and Grossmann (65) a considerable excess of PCl_3 was used (1 mol phenol chloride + 3 or 2 mols PCl_3) produced only slight quantities of monochloride.

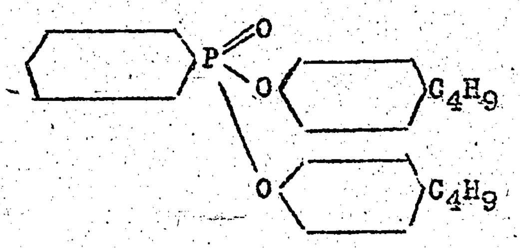
115 gr. monochloride were then heated with 11.5 gr. sulphur to 250° (65). The desired reaction then took place with heat and a brown colouration. The oil obtained was fractionated in a vacuum. After brief first runnings, the main bulk (120 gr.) was obtained at BP_{12} 230-260°. After a few days the chloride solidified spontaneously when it was extracted and washed with a little ether.

25. Phenyl phosphinic acid dicresyl ester.



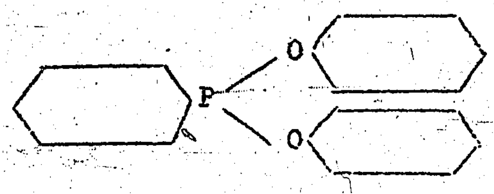
This ester was prepared in a similar way to the phenyl ester. The starting material used was phosphenyl chloride and a mixture of the three isomeric cresols in the proportions of 1:1:1. When the components were brought together there occurred a violent reaction and considerable generation of hydrochloric acid. It was stirred for 2 hours and then distilled. After a brief first running the ester was obtained at BP_{26} 255-278°, and the bulk was obtained between 270 and 272. From 55 gr. phosphenyl chloride and 100 gr. cresol there were obtained 55 gr. ester, i.e. 53% of the theoretical amount. The ester did not solidify on cooling to 0°. The boiling point at normal pressure was BP_{760} 390-400°.

26. Phenyl phosphinic acid di-p-butylphenyl ester



This compound was obtained by adding 17 gr. butyl phenol to 6.7 gr. phosphenyl chloride, after the latter had been chlorinated. The butyl phenol was prepared from p-butyl benzene sulphonate by fusing with alkali. To complete the reaction, stirring was carried out for 4 hours and then it was fractionated in a vacuum. After a brief first runnings the bulk was obtained between 260 and 318° at 20 mm Hg, the greatest amount being between 305 and 318°. The yield was 12 gr. = 76% of the theoretical amount. The ester, an oily liquid, is very much thinner than Preparation 25, a fact that is particularly noticeable at low temperatures.

27. Phenyl phosphinous acid diphenylester



This substance, which has not previously been described, may be obtained very easily by heating phosphenyl chloride and phenol. 50 gr. phosphenyl chloride are heated with 88 gr. phenol for 3 hours in the sandbath, the temperature being kept between 150 and 170°. The mixture is then distilled. First of all comes the first running and the excess phenol, then at BP_{13} 217-228° the desired ester. After rectification it boiled at BP_{15} 225-228°. The yield was 70 gr. = 85.5% of the theoretical amount. After a few days the ester solidified to form a colourless crystalline mass. 234.85 mg of the substance produced 90.85 mg. $Mg_2P_2O_7$ (Carius).

calculated P: 10.87, found P: 10.8%

3. Improving the solubility in oil of various additives

An inadequate degree of solubility in mineral oil was first ascertained in the case of diphenyl phosphate. Attempts were therefore made to improve solubility by choosing a solution aid. The latter must, of course, be such that the properties of the lubricant are not impaired, a fact which made high demands on the thermal behaviour.

The problem was to bring about the solution of a polar body, diphenyl phosphate, with a highly non-polar mixture of substances, the mineral oil. After a few experiments, we had recourse to lauryl alcohol. The latter has a relatively high boiling point, is soluble in oil and moreover readily dissolves diphenyl phosphate. This favourable two-way behaviour is to be attributed to the molecular structure, Lauryl alcohol contains both the polar hydroxyl group and the liophilic dodecyl part. A particularly favourable circumstance for a number of practical experiments was provided by a solution of 1 part diphenyl phosphate and 1 part lauryl alcohol; after heating to 120° to expel the water of crystallisation of the diphenyl phosphate, a homogeneous fluid was formed. This considerably simplified the solution of the additive.

The following is an extract from various solubility experiments:

Oil	Additive	Solvent (Tech. Lauryl alcohol from Deutsche hydrierwerke)	Heated to °C	Stood at °C	Finding
Shell AB 11	0.6%	--	150	20	cloudy
"	0.6%	--	150	-15	v. cloudy
"	0.6%	1.0%	150	20	almost clear
"	0.6%	1.0%	150	-15	slightly cloudy
"	0.6%	2.0%	150	20	clear
"	0.6%	2.0%	150	-15	almost clear
Essolub 40	0.3%	--	120	20	slightly cloudy
"	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	sl. cloudy
"	1.0%	--	120	20	v. cloudy
"	1.0%	0.7	120	20	clear
"	1.2%	1.5	120	20	clear

With Preparation 891 I.G., lauryl alcohol had a similar effect. Later on the question arose of stirring the preparations into the oil without heating. In the case of 1586/80 I.G. Dr. Brockstedt had already found that when 1586/80, benzol and spirit were mixed in proportions of 2 : 1 : 1, the cold stirring method could be adopted. According to our experiments, the preparation did not even form a block at -18°, at which temperature it was kept for 3 days.

In order to incorporate phenyl phosphinic diphenyl esters with oil in this easy way, we tested a large number of solvents. Experiments with benzene, toluene, carbon tetrachloride, ethanol, butanol, methyl ethyl ketone etc. were unsuccessful, and only the combination Ester : benzene :

ethanol in the proportions of 4 : 3 : 3 achieved success. This mixture, a thin oil, may be stirred cold into Rotring, without anything being precipitated at -15°.

Attempts were subsequently made to avoid the use of solvents and solution promoters by including suitable lipophil-creating groups in the molecule. This was completely successful in the case of the two preparations tried. By the reaction of phosphenyl tetrachloride with p-butyl phenol or a mixture of the 3 isomeric cresols, phenyl phosphinic acid di-p-butylphenyl ester and phenyl phosphinic dicresyl ester were made. Both are clear liquids, which can be mixed with the oil at room temperature in a concentration of 1.5%. It was not attempted to make higher concentrations.

The same process was also used for di-p-chlorophenyl phosphate. Derivatives were produced with a methyl, propyl, amyl and lauryl group in the nucleus. We will only mention here as a provisional finding that di-(2chloro 4butyl-phenyl) phosphate mixes with ligroin in the proportion of 1 : 1, while di-p-chlorophenyl phosphate will only dissolve up to 0.07% in the same solvent. These experiments are at present being carried out and completed by Mr. Fischer in connection with work for a diploma.

It has thus been demonstrated that solution-promoters were suitable for preliminary experiments, but having regard to the protracted storage, the final preparations must be made soluble in oil by the insertion of lipophile groups.

4. Investigation of blended oils

By adopting the most varied testing methods, a careful check on the lubricants was ensured. Without an oil-testing machine it is impossible to examine so many preparations, as engine tests entail great expenditure of time and material, and still do not afford a find degree of differentiation. It has been found that the results obtained with a wear machine of theSiebel-Kehl type agree very well with those obtained on the bearing test bench and in experiments with engines. The following equipment was used for the experiments :

a. - Wear-testing machine of the "Siebel-Kehl" type.
b. - Bearing test bench.
c. - Running tests with a 2.1 BMWvehicle
d. - Tests with aero-engines.
e. - Tests on the Four Ball apparatus.
f. - Ring sticking and other lubricant tests.

a) Testing with the Siebel-Kehl type of wear machine.

conducted by Dr. Brockstedt at the Staatl. Materialprüfungsanstalt of the Technical College, Stuttgart.

This apparatus works with purely sliding friction. The diagram of the test device, which is described in greater detail in my diploma thesis, will be seen from Fig. 15. The dimensions of the test pieces are also given. These are placed in a bath of lubricant, whose temperature is kept constant at 120°C and run with their ends towards each other. In order to attain high surface pressures, the lower, stationary test piece is recessed in the form of segments. The entire contact surface is 33 sq. mm. Whereas in these experiments the lower, stationary test-pieces are made of normally-annealed steel St.60.11, the upper test pieces consist of piston alloy EC 124, lead bronze or silver. At a sliding speed of v = 1 m/sec., the distance run per experiment and increment of load was made 2.0 km, corresponding to a duration of $\frac{1}{2}$ hour. The moment of rotation was recorded currently and the coefficient of friction calculated from it. Prior to the commencement of each series of experiments, the surfaces were carefully treated and then ran with a surface pressure of 120 kg/sq. cm. to start with. Dismantling, cleaning and evaluation of the abrasion was the next process, then remounting and filling with fresh oil. At intervals of 2.0 km run, the test pieces were loaded without dismantling until the sliding surfaces seized (sharp rise of the coefficient of friction). Fig. 16 shows a general picture of the machine, whilst the action of the addition of phosphenyl chloride is shown in Figs. 23-25.

Results :

The following results were all carried out with the pair of materials steel EC 124. With preparations where the optimum concentration was ascertained by a series of experiments, an "o" will be found after the percentage content. The oil used throughout was Rotring.

No.	Additive	Conc.	Max. load supported	Coeff. of fric. Start	Finish	
	Dibutylphosphite	1.0	450	low		
7	Diphenylphosphate	1.0 o	750-1000	<0.01	<0.01	+ 1% Laurylalcohol
1	Phenylphosphinic acid diphenyl ester	1.2 o	600-1000	0.02		
4	Phenylphosphinic acid monophenyl ester	1.0	450	low		
2	Phosphenylchloride	0.1 o	850	0.01	0.01	
36	Phosphenylous acid	0.3-0.4 o	750	0.01	0.01	
38	'#891' I.G.Farben	0.8 o	750	0.01	0.01-0.02	
	'#1534' "	1.0 o	450	0.04	0.08	
9	Di-p-chlorphenylphosphate	1.0 o	>1400	<0.01	<0.01	
9	" Heated 1 hr. to 200°	1.0	>1400	<0.01	0.02	
15	Diphenylethylphosphate	1.5	550	0.025	0.025	
49	Tricresylphosphate + oleic acid	1.5) 1.0)	450	0.02	0.02	
50	Tri-p-chlorphenylphosphate	1.0	150	0.08		
12	Di-2.4-dichlorphenylphosphate	1.0	500	0.02	0.08	
32	Diphenylchlorphosphine	0.4-0.5 o	950	0.01	0.01	
6	Isopropylbenzenedichlor phosphine	0.5	750	0.01	0.02	
13	Dicresyl phosphate	1.0	350	0.015	0.06	
48	Triphenyl thiophosphate	1.0	150	0.08		
22	Diphenyl thiophenylphosphate	1.0	180	0.06	0.08	
16	Di-p-chlorphenylphosphoric acid methyl ester	1.0	1400	0.02	0.02	contaminated with chlorine
	"	0.5	850	0.01	0.01	

No.	Additive	Conc.	Max. load supported	Coeff of fric. Start	Coeff of fric. Finish	
10	Di-p-bromophenyl-phosphate	1.0	1100	0.01	0.02	
21	Di-p-chlorphenyl-thiophosphate	1.0	1050	<0.02	<0.02	
20	Diphenyl thiophosphate	1.0	800	<0.02	<0.02	
8	Di-p-nitrophenyl-phosphate	1.0	550	0.02	0.08	
17	Di-p-chlorphenyl-phosphoric acid	1.0	1400	0.02	0.02	contam.
	propyl ester ""	1.0	150	0.08	0.08	purified
18	Di-p-chlorphenyl-phosphoric acid lauryl ester	1.0	150	0.04	0.08	
11	Di-p-fluorphenyl-phosphate	1.0	1400	0.01	0.01	
14	Di-p-chlorphenyl-phosphoric acid monochloride	1.0	950	<0.01	<0.01	
	" heated 1 hour to 300°	1.0	150	0.08		
	"	0.5	650	0.01	0.01	
3	Phenylphosphinic acid di-p-chlorphenyl ester	1.0	500	0.04	0.06	
5	Phenylphosphinic acid mono-p-chlorphenyl ester monochloride	1.0	650	<0.02	<0.02	resinified
23	Diphenylphosphoric acid sulfochloride	1.0	300	0.03	0.04	
24	Di-p-chlorphenyl phosphoric acid sulfochloride	1.0	550	0.04	0.07	
	Phenylphosphinic acid diphenyl ester chlorinated	1.0	450	0.04	0.07	
42	Sulfur	0.008	450	<u>0.10</u>	0.14	x
41	Diethylamine-N-sulfo-chlorphosphine	1.0	150	0.08		
40	Monoethylaniline-N-oxychlorphosphine	1.0	200	0.04	0.08	
25	Phenylphosphinic acid dicresyl ester	1.5	850	0.02	0.08	
26	Phenylphosphinic acid di-p-butylphenyl-ester	1.5	750	0.04	0.09	
27	Phenylphosphinous acid diphenyl ester	1.0	900	0.04	0.04	

x Higher concentrations were also investigated. These, however, revealed a very much inferior behaviour. Experiments with lower concentrations have been started.

The following were without effect:

a) diphenyl phosphinic acid, whose solubility behaviour is too poor.
b) Oxyphosphazobenzene anilide (0.5%).
c) Races prepared with diphenyl phosphate in xylol.
d) 3% methyl salicylate (can be purchased from Schuchardt, Görlitz),

as indicated by Evans & Elliot (141).
e) 2% benzene sulphochloride, patented by the Gulf Oil Co. (142). The preparation was made from benzene sulphonic acid by the Gattermann method (143).
f) Naphthalene tetrachloride, patented by Evans (144), made from naphthalene according to Schwarzer (145).
g) Chlorinated diphenyl sulphide in 1% solution, mentioned by the General Electric Co (146), made from diphenyl sulphide (146).
h) Monochlorthianthrene, made by Fries and Vogt (147).
i) Diphenyl sulphide made according to Hartmann, Smith and Dickey (148)

b) Bearing test-bench experiments in the machinery laboratory of the Technical College, Stuttgart, Forschungsinstitut für Wärmekraftmaschinen (Prof. Wewerka).

This test-bench is of considerably larger dimensions than the Siebel-Kehl machine and marks a transitional stage to practical application. The machine is illustrated in Wewerka's report (138), and a diagram of the testing device is given by Väth (139). The machine can be loaded up to 10 tons, so that pressures up to 100 kg/sq. cm. are obtained. The load on the bearing is hydraulic by means of 2 oil pistons. The diameter of the bearing is 45 mm and length 20 mm. At a speed of 3000 revolutions of the driving motor, a sliding speed of 7 m/sec is obtained. The test shaft consists of nitrided steel and is polished and lapped. The diametric play of the bearing is 0.09 mm (see Fig. 17). The material of the bearing shells may be changed. On attaining the limiting load, the temperature of the bearing rises sharply and the test machine is stopped by the safety device on the driving motor.

As Wewerka and his colleagues found, the spec. load capacity rises parabolically with the lubricating oil pressure, over a wide range with $\sqrt[3]{p}$. When recorded on double logarithm paper, the curve is rectilinear. This makes it possible to check the accuracy of the experiments (Fig. 18) and this method has therefore been used in experiments with our preparations. On testing, the following results were obtained. The table gives the spec. load capacity of various bearing materials at a lubricating oil pressure of p = 1 atm abs. the conditions being those given above :

Lube oil B C 8 4.5° Engler/50°C	Lead-Bronze kg/cm2	Silver kg	Special Brass kg	Light metal M 124 kg
pure	270	390	300	600
0.05% Phosphenylchloride	490	500	140	---
0.3 % phosphenylic acid	450	740	350	700
0.6 % 891 I.G. Farben	410	1200	440	780
1.2 % Phenylphosphinic acid diphenyl ester	780	470	1000	760

These figures show that qualitative agreement is achieved to a very great extent with the results on the Siebel-Kehl machine. Fig. 18 shows the dependence of load on oil pressure, Fig. 19 the effect of additives on the temperature of the bearing. The final temperature on attaining the limiting load (critical bearing temperature) is equally high with the various admixtures, but the action on load capacity varies considerably with the different bearing materials.

c. Running tests with a 2 l BMW motor vehicle

conducted by Prof. Glocker, Institut für Metallphysik at the Kaiser-Wilhelm-Institut für Metallforschung, Stuttgart.

During heat tests on blended oils, a considerable drop in efficiency was found here and there. Protracted experiments on the Siebel-Kehl wear machine at 120°C and on the bearing test branch only indicated a slight drop. To elucidate these conditions, which are of great importance in practice in the engine, running tests were carried out with a 2 litre BMW motor vehicle. Oil was taken before starting and after given laps in the journey, and this oil was tested on the Siebel-Kehl machine. It was found that the efficiency declines rather rapidly to start with and subsequently falls gradually (Fig. 6 and 7). The distances given were covered without the addition of fresh oil. When the additive was topped up (Fig. 7 and 8) the original efficiency was restored, and this again declined.

For an assessment of the lubricants, in addition to the coefficient of friction, the surface pressure withstood was also of decisive importance; this is the pressure at which no seizing of the sliding surfaces has yet occurred. Falling values for surface pressure and rising coefficients of friction point to a drop in the efficiency of the additives. It must however be borne in mind that the coefficient of friction with many additives, even at slight pressures scarcely alters up to seizing point (diphenyl phosphate).

Whether the drop in efficiency is due to a reaction of the additive with the lubricating oil or the metal parts to be lubricated, is not yet quite clear (see introduction). Purely thermal decomposition which only occurs to any extent in the vicinity of the combustion area, should not be the deciding factor, since the best additives attain approximately the thermal stability of the lubricating oil itself.

Experiments with a stationary single-cylinder NSU engine 201, carried out at the Forschungsinstitut für Kraftfahrwesen, Stuttgart, (Prof. Kamm), presented a similar picture (Fig. 9).

d. Experiments with aero-engines.

conducted by Messrs. Daimler-Benz.

In the aero-engine conditions are more favourable than in the case of the automobile engine, insofar as fresh oil has to be added from time to time and the falling values of the surface pressure do not therefore drop below a constant mean value. In the automobile engine, as is well known, the oil is only changed at long intervals. The results of experiments with different additives are shown in Fig. 10-14. The original efficiency is not completely maintained in any of the three additives examined.

With diphenyl phosphate (Fig. 15) after about 5 hours in the main engine a drop to $p \simeq 350$ kg/sq cm occurred, a figure which does not fall any more during further operation. The pressure withstood for Rotring oil without additive under these conditions, with a very much higher coefficient of friction, amounts to about 150 kg/sq cm

Even after 3 hours phenyl phosphinic acid diphenyl ester gives a mean pressure figure of 325 kg/sq cm (Fig. 11,12). In contrast to diphenyl phosphate, in which the coefficient of friction remains 0.025 here it rises with the drop in the pressure withstood and in the most unfavourable case amounts to 0.07.

The decline in the effect in the single cylinder engine (Fig. 11, 13 and 14) proceeds very much more slowly than in the main engine, a fact that is probably to be attributed to the higher thermal stress in the latter.

With Additive 891 there occurred after the initial drop in efficiency a slight rise. There was then set up a mean surface pressure carried of 500 kg/sq cm and a coefficient of friction of 0.025. The renewed rise took place after the first addition of a large quantity of fresh oil.

Series experiments with IG 891 then demonstrated the action of these preparations when running-in. The seizing of bearings, which is usually such a feature and wastes so much time, was lacking.

e. <u>Tests in Boerlage's four-ball apparatus</u>

conducted by Mr. Glaubitz, Chief Engineer, at the Staatl. Materialprüfungsanstalt of the Technical College, Stuttgart.

Experiments with sulphurised oils (also gear oils), in contrast to those on Boerlage's four ball apparatus and in highly stressed gears, showed only slight improvement, or else no improvement at all when tested on the Siebel-Kehl machine. In order to provide means of comparison and possibilities of further tests, and, more especially to get to know something about the chances of using ourpreparations for gear oils, at Dr. H. C. Brockstedt's instigation, tests were carried out on the four-ball apparatus.

The four-ball apparatus was evolved by Boerlage (135) in 1933 with the Bataafsche Petroleum Maatschappij at Delft, in order to test extreme pressure lubricants. Its special advantage lies in the use of steel balls as test pieces, which can be obtained cheaply and with a uniformity that had not hitherto been attained. In the course of years it was found that the figures obtained with this device agreee particularly well with the conditions occurring in gears and other gear lubricant apparatus (see Seemann 136)

The apparatus was tested in 1941 by the Rhenania-Ossag (136) and subsequently by the DVL (137) and experimented with anew. The friction element consists of 4 steel balls arranged in pyramidal form (Fig. 4), 3 of which are attached to the experimental cup by means of a collet and screw cap. The cup also contains the lubricant to be tested. The fourth ball is fastened in a chuck, which is connected by a spindle to the shaft of the electric driving motor (Fig. 5). The housing carrying the motor can be loaded from below by means of a system of levers, and the load is finally transferred to the lubrication points. The coeffieint of friction is measured by an indicator spring.

In the experiments in the Material Testing Institute, steel balls or bonded (phosphatised) steel balls were used. The use of phosphatised balls as the result of preliminary experiments by Daimler-Bezn A.G. (Dipl.Ing. Bokemüller and Dr. Seemann). The balls run for a minute at a determined load. They are then dismantled, cleaned and the spherical indentation caused by wear is measured. Measurements are carried out in the direction of running and in the direction at right angles thereto and the mean value for the 3 lower balls is plotted against the load. The fourth ball exhibits a circular ring of wear, to which no further attention is paid. The point of seizing is the point at which there occurs sudden increase in friction and wear (Fig. 5a). At the welding point, the balls are firmly welded together. Other terms, such as crack point (Sprungpunkt), active point are not considered, as they require clarification.

Results on 4-ball machine (Steel balls)

Type of oil	Additive %	Seizing point by load	Welding point by load
Rotring Motor-oil	-	110	180
Army Summer	-	100	200
Essolube E 20	-	110	180
MOAS	+ 1% Diphenylphosphate	160	200
"	+ 0.8% 891 (I.G.)	240	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 + 1.0 % Laurylalcohol	170	200
"	+ 0.5% 14/135 (I.G.)	130	180
"	+ 0.5% 14/104 (I.G.)	150	180
"	+ 0.1% Phosphenylchloride	150	180
"	+ 0.4% Diphenylchlorphosphine	110	180
"	+ 1.5% Triphenylphosphine + 1.0% Tristearine	110	180
"	+ 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	250	280
"	+ 1.0% M 100 heated 1 hr at 200°C	200	240
"	+ 1.5% Phenylphosphinic acid diphenyl ester	90	180
"	+ 0.5% 1586 (I.G.)	150	170
"	+ 1.0% M 40$_1$	190	240
Hypoid oil (136) sulphurised		~1000	~1000

Phosphatised Steel Balls

Type of oil	Additive %	Seizing point by load	Welding point by load
Rotring	-		340
MOAS+	-	-	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 (I.G.)		700
"	+ 1.0% Diphenylphosphate + 1.0% Laurylalcohol	-	600
"	+ 1% M 100	850	950

f) Ring seizing and ageing tests, conducted by the Technical Research Station of the I.G. Oppau (Dr. Penzig).

Whereas phenyl phosphinic acid diphenyl ester behaved less favourably in the ring sticking test than preparation I.G. 891, it gave altogether better figures in ageing tests. It must be borne in mind that for the ring seizing tests, extreme engine conditions were applied. On the other hand, the ageing tests cannot immediately be applied to engine conditions.

	Rotring			
Unused oil	without additive	+ 0.6% 1586/80	+ 1.2% Ester	+ 0.6% 891
Viscosity in cSt				
38°C	263.5	262.5	250.5	270.3
99°C	19.25	18.90	19.01	19.3
Conradson test %	0.35	0.26	0.21	0.32
Neutralisation No.	0	0.81	0.18	0.25
Saponification No.	1.01	1.58	1.72	1.45
Used oil				
BMW Exper. No.	695	693	691	694
Viscosity in cSt				
38°C	268.5	195.5	256.5	219.9
99°C	18.14	15.76	18.95	16.94
Conradson test %	0.77	0.60	0.46	0.68
Neutralisation No.	0.36	0.78	0.51	0.67
Saponification No.	0.91	1.35	2.64	1.98
Ageing test (Brit. Air Min.)				
Loss %	3.8	3.8	2.0	6.4
Viscosity in cSt				
38°C	369.5	450	339.6	774
99°C	25.0	27.2	22.4	37.4
Thickening at 38°C in %	41	71	29	195
Conradson test	4.59	2.49	1.24	3.44
Asphalt	0	0	0	0

5. Phosphorus compounds which are given in technical literature as additives for lubricants

It is worth noting the materials which have laready been used as additives to lubricants. For the sake of clarity, these have been divided into three classes:

1. Derivatives of the phosphoric acids.

II. Phosphines.

III. Other phosphorus compounds.

First figure after the patent holder: Literature reference is bibliography

Second figure after the patent-holder: Year of the patent application

Third " " " " " " " " " granted

Fourth " " " " " " " " priority

1. Derivatives of phosphoric acids.

Standard Oil Development Co. 66/1934/1935/1933

A turbine oil with high flash and self ignition points, consisting e.g. of tricresyl phosphate.

Atlantic Refining Co. 67/1934/1935/1933

Mineral oils with up to 10% of an organic phosphoric acid triester, which can contain alkyl and aryl groups, are used as extreme pressure lubricants. The combinations may also be halogenated. Test carried out on the Timken testing machine.

E.J. du Pont de Nemours & Co. 68/1934/1935

Acid esters from ortho, meta or pyrophosphoric acids, from phosphoric acid and hypophosphoric acid with alcohols and phenols enhance the effect of pressure lubricants.

E.J. du Pont de Nemours & Co. 69/1934/1935

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

Socony Vacuum Oil Co. 70/1935/1936

To prevent the corrosion of metal surfaces, consisting of Cd, Ag, Cu or Pb alloys, the mineral lubricating oils are given an additive consisting of 0.1-1% triphenyl phosphite.

Socony Vacuum Oil Co. 71/1935/1936

To prevent corrosion, tricresyl phosphite is added to mineral oils in the proportion of 0.1-1%

Socony Vacuum Oil Co. 72/1935/1936

0.05-2% of a triaryl phosphite are used as anti-oxidants for hydrocarbon oils.

Celluloid Corp. 73/1935/1937/1934

Lubricants from a mineral or vegetable oil are mixed with an emulsifying agent and a neutral ester of phosphoric acid. The ester contains at least one aryl group. Esters of thiophosphoric acid may also be used. The lubricants are particularly suited for high pressures and speeds.

Standard Oil Development Co. 74/1934/1937

Lubricating or insulating oils consist of an ester of phosphoric acid, such as tricresyl phosphate to which further antioxidants are added.

Standard Oil Co. 75/1936/1937

In order to prevent corrosion in certain bearing metals, the lubricating oil is improved with a mixture of mono, di and tri-alkyl phosphites.

Canadian Industries Ltd. 76/1935/1937

In order to avoid seizing, bearings are lubricated using aliphatic esters of phosphoric acid. The esters react with the surface of the bearing.

Continental Oil Co. 77/1936/1937/1935

Mineral oils are mixed with a small quantity of a phosphoric ester of an aliphatic or aromatic thiophenol or thioalcohol

Standard Oil Development Co. 78/1937/1938/1936

Liquid organic esters of phosphoric acid (tricresyl phosphate) are used as lubricating oils for precision apparatus.

A. Foulon 79

Phosphoric acid esters are used as anti-corrosion extreme pressure lubricants.

E.J. du Pont de Nemours & Co. 80/1937/1938

Additives for high pressure lubricants are obtained from naphthenic (Naphthenyl) alcohols ~~and derivatives~~ of phosphoric acid, such as PCl_5, $POCl_3$, PCl_5 $PSCl_3$ etc.

Atlantic Refining Co. 81/1936/1939

Mineral oils acquire extreme pressure properties if compounds are added to them which are prepared from PCl_3, PCl_5, $POCl_3$, $PSCl_3$, P_2S_3, P_2S_5 with primary or secondary amines. (e.g. $ClC_6H_4{-}NHPOCl_2$)

Standard Oil Development Co 82/1938/1939/1937

Lubricating and insulating oils obtain by the addition of thio or seleno esters of phosphorous acids a certain stability at high temperatures.

Standard Oil Development Co. 83/1938/-/1937

Additives of 0.02-5% of an organ. thiophosphite impart a high degree of resistance to oxidation to lubricating oils.

Socony Vacuum Oil Co. 84/1938/1939

Organic phosphites and thiophosphites impart to mineral oils some improvement in regard to pressure properties and resistance to oxidation. Hydrolysis is prevented by the addition of amines.

Socony Vacuum Oil Co. 85/1938/1939

Additions of condensation products from PCl_3 and amines, which still have a free H-atom in the nucleus, prevent corrosion and impart extreme pressure properties.

Curt Ehlers 86

Additions of tricresyl phosphate to engine oils results in corrosion owing to the phosphoric acid released

Standard Oil of California 87/1937/1939

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

C.M. Larson 88

As oiliness additives for aero engines, phosphates may also be used. Lead phosphate is formed in the exhaust.

Standard Oil Development Co. 89/1938/1939/1937

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

Standard Oil Co. 90/1937/1939

Highly refined oils are improved as regards their corrision behaviour by the addition of chloro-alkyl phosphites (prim. sec. and tert.) Chlorination takes place for preference in the beta or alpha position.

E.J.du Pont de Nemours & Co. 91/1936/1939

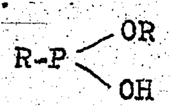
The corrosion effect of oils on Cd-Ag alloys is prevented by the addition of alkyl, aryl or aralkyl phosphates.

Atlantic Refining Co. 92/1937/1939

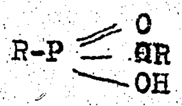
In order to improve the film rupture strength, aliphatic or aromatic phosphates, phosphites or thiophosphites can be added to oils.

Standard Oil Co. 93/1936/1939

To decrease corrosion, oil is treated with phosphinites and phosphinates:



$R-P(OR)(OH)$



$R-P(=O)(OR)(OH)$

E.J. du Pont de Nemours & Co. 94/1937/1939

By the addition of naphthenic esters of phosphoric acids, mineral lubricating oils are improved in regard to extreme pressure properties, corrosion and the formation of sludge. These combinations have a better effect than the corresponding esters of the aliphatic alcohols or phenols.

General Electric Co. 95/1936/1939

Alkyl phosphates areused in oil mixtures.

Gulf Oil Corp. 96/1938/1939

Phosphoric esters that are soluble in oil improve mineral lubricating oils for explosion engines.

N.V. de Bataafsche Petroleum Mij. 97/1939/1940

Lubricating oils are improved as regards their high pressure properties by the addition of phosphoric esters of the formula $R-O-P(Halogen)_2$. Corrosion does not take place.

Standard Oil Co. of California 98/1939

Metal salts of substituted phosphoric acids improve lubricating oils as regards their resistance to heat. They also prevent piston rings from sticking.

Standard Oil Development Co. 99/1939/1940/1938

Products from phosphoric halogenides and olefins, terpenes etc. impart extreme pressure properties to lubricants.

E.J. du Pont de Nemours & Co. 100/1938/1940/1937

Film strength, lubricating capacity, resistance to corrosion and oxidation in lubricating oils are improved by the addition of mono, di and triesters of phosphorous or thiophosphorous acid. The acids are esterified with branched aliphatic alcohols of 6-9 C atoms.

E.J. du Pont de Nemours & Co. 101/1938/1940/1937

The same improvement as under "100" above is shown by the addition of alkyl thiophosphites, whose alkyl groups are connected direct with the S- atoms.

Atlantic Refining Co. 102/1938/1940

Lubricating oils are heated with 0.25-50% tricresyl phosphite or another organic compound with trivalent phosphorus. A portion of the reaction products formed remains in solution in the oil.

Gulf Oil Corp. 103/1938/1940

$POCl_3$ is allowed to act on alkylated phenols in the presence of small quantities of P_4S_3 and the products obtained are added to mineral lubricating oils. The high pressure properties, resistance to oxidation and corrosion are improved and the sticking of the piston rings is prevented.

I.G. Farbenindustrie A.G. 104/1937/ 1941.

Lubricants from polymerisation products contain tributyl phosphate, tri-p-chloroethylphosphate etc.

Lubri-Zol Corp . 105/1938/1940

To mineral oils are added, inter alia, metallic salts of condensation products of triphenyl phosphate, triphenyl phosphite, tricresyl-phosphate with substituted fatty acids.

Atlantic Refining Co. 106/1936/1940

Tricresyl phosphate, butyl phosphate and other esters are used as solvents for additions of thiouea to lubricating oils.

Musher Foundation Inc. 107/1939/1940

Lubricating oils with decreased corrosion and sludge formation are obtained by the addition of 0.1-0.3% of a mixture of aryl phosphites with lecithin and protracted heating to at least 175°.

Standard Oil Development Co. 108/1939/1940/1938

Additions of 0.1-2% tert. ester of phosphorous and thiophosphorous acid to lubricating oil, increase slipperiness and resistance to temperature and oxidation and decrease the tendency to fouling and carbon deposition.

Texas Co. 109/1939/1940

Lubricating oils are improved by the addition of tertiary, alicyclic phosphites. The separation of di and triphosphites is carried out by distillation in a vacuum.

Standard Oil of California 110/1938/1940

To mineral oils added metallic salts of various phosphoric acids, whose H-atoms are replaced by various radicals.

Gulf Oil Co. 111/1936/1940

Non-corroding, oxidation resisting extreme pressure lubricating oils are obtained by adding alkyl phenol phosphite, -thiophosphites and phosphates. The alkyl phenols are obtained from olefins and phenols in the presence of sulphuric acid.

Standard Oil Development Co. 112/1939/1941/1938

Additions of fatty acids and other materials, such as phosphites and phosphates, improve mineral lubricating oils.

Texas Co. 113/1939/1940

Improved lubricating oils for I.C. engines contain 0.01-2% tri, di or monophosphites, especially of cyclo hexanol.

Shell Development Co. 114/1938/1940

Preparations which are obtained by the reaction of PCl_5 and $POCl_3$ with tertiary alcohols impart extreme pressure properties to lubricants.

Standard Oil Development Co. 115/1938/1941

To improve lubricating oils, phosphite esters of a determined configuration are used.

Tide Water Associated Oil Co. 116/1939/1941

Mineral oils are stabilised by the addition of 0.1-2% of a phosphite ester of a thiophenol.

Richard Israel Levi 117/1939/1940

Castor oil is converted by reaction with phosphoric halogenides into oil soluble phosphoric esters and these esters improve mineral lubricating oils.

Walter G. Whitman 118

Alkyl phosphates are added to improve lubricating oil in the engine.

Monsanto Chemical Co. 119/1938/1940

Trihexyl phenylphosphite and phosphate are used as additives for lubricants.

Standard Oil Development Co. 120/1936/1940

Tricresyl phosphate is used among components for making an compounded oil.

Standard Oil Co. 121/1936/1940

Anti- corrosive additives to mineral oils consist of alkyl or aryl mono, di or trithiophosphites.

Ohio Oil Co. 122/1938/1941

Mineral ~~lubricants~~ oils acquire extreme high pressure properties by the addition of up to 3% compound, such as butyllauryl or cresyl ester of phosphoric and phosphorous acid.

Lubri-Zol Corp. 123/1937/1939

Organic phosphorus compounds (esp. esters of the various phosphoric acids) are used as anti-corrosives in extreme pressure oils.

Lubri-Zol Corp. 124/1937/1941

Lubricating oils receive extreme pressure properties by the addition of 0.1-2% halogenised, aromatic thiophosphates, which have at the same time an anti-corrosive effect.

Texas Co. 125/1939/1941

Mineral oils contain an addition of a phosphite ester. The acid is esterified with alkyl ethers of alkylene glycols.

Canadian General Electric Co. Ltd. 126/1937/1941

A reduction in the viscosity of oils is obtained by adding 25-50% of an alkyl phosphate. The alkyl contains no more than 4 C-atoms.

Celluloid Corporation. 127/1934/1941

A steam turbine oil contains in addition to chlorinated diphenyl some 50 parts of triaryl phosphate.

II. Phosphines.

NV de Bataafsche Petroleum Mij. 128/1937/ 1937/ 1936

Complex compounds which, in addition to an inorganic component, contain e.g. a tertiary phosphine (triethyl phosphine), and are suitable as additives for lubricating oils.

Atlantic Refining Co. 129/1936/1938

Mineral oils are improved in their extreme pressure properties, lubricating and coefficients of friction by the addition of phosphine oxides and sulphides

Atlantic Refining Co. 130/1936/1939

Additions of 0.1-5% of organic phosphines impart to mineral oils extreme pressure properties, e.g. tripyridyl phosphine, monophenyl and diphenyl phosphine.

Sun Oil Co. 131/1937/1940

Additions of propyl benzene and butyl benzene dichlorophosphine improve high pressure properties.

Atlantic Refining Co. 102/1938/1940

Instead of tricresyl phosphite, tributyl phosphine, triphenyl phosphine etc. may be used.

Standard Oil Development Co. 132/1940/1941/1939

To decrease the formation of sludge, 0.1-5% phosphine are added: triphenyl phosphine, monophenyl phosphine, tolyldiisobutylphosphine. The phosphines may also contain N,S,O and Cl.

Texas Co. 133/1939/1941

Additions of phosphinic acid esters are used

Cities Service Oil Co. 134/1939/1941

Additions consist of condensation products of organic phosphines or chlorophosphine oxides

Standard Oil Co. 93/1936/1939

For improving the corrosion behaviour of oils, triphenyl phosphine oxide and sulphide are added.

III. Further phosphorus compounds

(These are briefly mentioned with the bibliographical reference, and the glycerine esters are included here).

C 38/1/4407 $(PnCl_2)_x$

C38/11/ 1168. Reaction product of nitriles and P_2S_5.
C38/1/1945 Phosphatides.
C/39/11/975 P or phosphides are heated in oil
C/39/11 976 Organic P-compounds
C/39/11/2195 P in heteroxycl. rings

C/39/11/4634	Substances having P in the ring
C/40/1/2110	Product of P_2S_3 and phenols or olefins
C/40/1/24	Treatment of the oil with $PSCl_3$ and filtering.
C/40/2700	Phosphorus sesquisulphide.
C/41/1/608	"Phosphorised" ~~oils~~
C/41/1/608	Phosphoric acid
C/41/1/1633	Phosphatides
C/41/1/1535	Lecithin, cephalin
C/41/1/2208	"phosphorised" fatty oils.
C/41/1/2419	Lecithin.
C/41/1/2489	Phosphatides
C/41/1/2701	Phosphatides
C/41/11/566	Additions of alkyl thiocarbonates and phosphoric halogenides.
C/42/1/419	Phenol derivatives of $PNCl_2$
C/42/1/1330	Phosphatides
C/42/1/3164	Amorphous phosphorus heated with oil
C/43/11/1777	Phosphatides
C/43/11/2130	"phosphorised" fatty oils
C/43/11/2131	Phosphatides.
C/44/1/406	P-compounds that are soluble in oil.

So far as is possible on the basis of our experience, I should like to give a brief appreciation of the foregoing patents. First of all I should like to state that we carried out our development work practically without reference to patent literature, owing to the fact that the results which are utilised there were obtained with quite different testing apparatus and are therefore not comparable with our own.

Neutral phosphoric esters, as given in 67, produced no effect with us, although acid esters, indicated in 68 and 69, did so. According to a private communication from Dr. Zorn (I.G. Leuna) to Prof. Glocker these esters (diphenyl phosphate) were previously introduced into the United States Air Force. The tertiary esters and thiophosphoric acids described in other patents will not be further discussed. In 76 it is stated that aliphatic esters react withthe surface of the bearing in certain lubricating conditions a view that is also shared by ourselves. The esters of the thiophenols and alcohols, to which preference is given in 78, according to our experiments did not show any improvement compared with the esters containing oxygen. The amines mentioned in 81 and 85 were found by us to be inactive. The dihalogenides indicated in 97 are eaily decomposed by water and therefore unsuitable. Metal salts of substitued phosphoric acids (98) are, according to our experiments, on the whole insoluble in oil. The reference in 103, that piston ring sticking is prevented by the addition of esters, is remarkable. Phosphites (113), which are frequently mentioned, did not produce any very great activity in our experiments. The phosphines mentioned in 128 and 129 will not, in all probability, bring about any improvement in the high pressure properties. Dichlorophosphine (131), despite what is said to the contrary, is decomposed by water. The phosphatides mentioned in Section III were not closely investigated by us. Phosphorus heated with oil certainly improves the pressure characteristics. By this means dark coloured oils and resinification are, however, obtained. We found that phosphoric acid itself is without effect.

Taken on the whole, we have here a mass of somewhat contradictory statements. Nevertheless, one must reckon on the fact that in US A, whence most of the patents originate some of the preparations must have been used in practice, and it is surprising that so far so little work has been carried out in this direction over here.

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Figs. 4 and 5 are taken from an article by Krienke, Oel und Kohle 40/19 (1944), 5a from Seemann, Oel und Kohle 40/19 (1944), 6-16 20, 23-25 are by Dr. Brockstedt of the State Material Testing Institute of the Technical College, Stuttgart (see page 2), 17-19 by Prof. Wewerka. Machinery Laboratory of the Technical College (see page 8) and 21-22 by Prof. Glocker, Institute for Metallo-Physics at the Kaiser-Wilhelm Institut für Metallforschung, Stuttgart.

7.

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