

INVESTIGATION OF PISTON-RING STICKING IN HIGH-DUTY AERO-ENGINES.

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SUMMARY.

A theory of the mechanism of ring-sticking due to oil deterioration, from the physico-chemical aspect, is presented, with due note of the mechanical factors involved.

Ring-sticking is due mainly to the wedging action of carbonaceous "coke-like" substances formed in the grooves by decomposition of products of oil deterioration. There appears to be a critical and optimum set of conditions under which ring-sticking takes place. Under such conditions a maximum amount of asphaltenic substances are formed and coked.

A consideration of the asphaltic systems leads to the conclusion that flow behaviour of the deteriorated oil, and the nature and proportion of the intermediate products of oil deterioration are the governing factors in ring-sticking, mechanical conditions remaining constant.

INTRODUCTION.

WHILE the severity of the conditions to which an aero-engine lubricant is exposed has increased manyfold with the increasing power output of aero engines in recent years, no parallel development in the production of lubricants which can stand up to such drastic conditions has yet taken place. Over-refinement of oils, such as by exhaustive solvent treatment, has been found to be a drawback rather than an advantage in the manufacture of a stable lubricant. It is now generally believed that over-refinement removes certain unknown natural oxidation-inhibitors, "retarders" or detergents or "peptizers" native in the oil, thus causing the highly refined oils to be less stable to heat and oxidation than the mildly refined oils.^{1,3} At one time, the aromatics or certain aromatic constituents present in the oil were believed to be the natural inhibitors.² Recent workers, however, have tried to correlate the stability of oils towards oxidation to natural sulphur compounds present in the oil.³

The fact remains, however, that from the consumer's point of view, lubricant has to be chosen for particular duties in different types of engines. Many chemical tests have been devised for rating lubricants. The mechanism of oil deterioration in the internal-combustion engine is very complex, and despite a large amount of work done on the subject, much remains to be discovered.

These chemical tests can be divided into three main classes :

- (1) Oxidation at low or moderate temperatures⁴;
- (2) Alteration on pure thermal treatment⁵;
- (3) Thermal-oxidation tests.⁶

The first class may have significance for crankcase conditions,⁷ but have no apparent relation to the cylinder wall and piston conditions of a high-duty aero engine. The carbon residue tests may have some significance

for sludging conditions. More recent thermal tests involve the determination of various physico-chemical changes of the oil on pure thermal treatment. The last-named class of tests are perhaps more towards approaching engine conditions than other. It is not the purpose of this paper to discuss the mechanism of oil deterioration, or the multitude of papers published in this connection. It is sufficient to point out that none of these tests have succeeded in their purpose, viz., to rate oils according to their behaviour in the engine, especially to their ring-sticking tendencies. Full-scale expensive engine tests still remain the only satisfactory means of rating oils for service.

RING-STICKING.

Of all the effects of oil deterioration, ring-sticking is perhaps the most dangerous, and the amount of work being done on the subject is sufficient proof that the prediction of this phenomena is sufficiently urgent and complex to warrant such effort. This paper deals only with the chemical aspect of the complex problem of ring-sticking.

Assuming the mechanical conditions remain the same, ring-sticking is a function of oil deterioration, produced by the physico-chemical conditions in the engine. The importance of mechanical variables, *e.g.*, ring side clearance, uniformity of clearance, ring conformation against the cylinder wall, material design and reproducibility, influencing ring-sticking is obvious and has been stressed by others.^{8,9} Any chemical method of rating oils can be tested properly by engine trial, only when these factors and oil consumption are closely controlled. The cause and nature of the phenomena have, however, remained obscure and controversial.

The two basic chemical changes which lead to the formation of piston deposits are (1) the oxidation of hydrocarbons, and (2) the thermal coking of the hydrocarbons under non-oxidizing conditions.

Tests based purely on one or other of these principles have failed to produce satisfactory results. It is realized that the final effect of these two basic changes may be influenced by other factors, *e.g.*, reactivity of the carbonized oil, volatility, asphalt solubility power of the oils, stability of suspensions of particles in the oil, response to catalysts, etc., which have been enumerated in detail by Von Philippovitch.¹⁰

Oils can be rated by any chemical method under the particular conditions of the test, and some very efficient tests have been evolved, *e.g.*, B.A.M. oxidation test, Indiana and D.V.L. oxidation tests, Ramsbottom and Conradson coke numbers, oxygen absorption, etc. However, the survey of literature showed that before the requisite chemical test could be evolved it would be necessary to discover the actual mechanism of ring-sticking and under what conditions it takes place and by what type of substances it is caused. It was also evident that the cause of ring-sticking must be sought for, not merely in the quantity of deterioration products formed under some arbitrary conditions, nor in sludging, but in the nature, composition, and proportion of these products and their physical behaviour under various conditions.

The macroscopic, microscopic, and chemical evidence which leads to the postulation of a tentative theory of ring-sticking as presented in this report, is given below.

Experimental work.

Deposits have been examined from pistons with stuck rings from liquid-cooled engines which have been operating in service, and from air-cooled single-cylinder engines which have been running on type oil tests to D.T.D. 472 specification, at R.A.E. The condition of the pistons as received is given in Appendix I.

Two forms of sticking may be distinguished, termed "hot stick" and "cold stick." In the latter case the rings are free whilst the engine is running but may be held in the groove by the setting of the groove deposit due to differential contraction when the engine is shut down and allowed to cool. On re-starting the engine the rings may be freed by re-melting of the deposit. In the case of "hot stick," however, the rings are held whilst the engine is running and the "stick" here is irreversible unless the deposit is burnt away; or if the deposit be brittle, it may be eroded away by ring-rotation. Thus it is possible to imagine that intermittent and incipient "cold sticks" may develop in the top rings, but may not finally affect the freedom of the rings. It is clear that it is the "hot stick" that one wishes to evaluate and were it not inherent that "cold stick" may, under more drastic conditions, lead to "hot stick" the former could be disregarded from the service point of view.

These two forms of sticking can be confirmed in the laboratory by testing the freedom of the rings at various temperatures. In a recent note¹¹ it has been shown that, with the pistons tested, the temperature at which the rings could be freed varied considerably. Those cases where the rings can be freed below 200° C. may be regarded as "cold sticks," whilst others in which the rings cannot be freed even at 300° C. can be safely regarded as "hot sticks."

It has been noticed at R.A.E. that both forms of "stick" may be present in the same piston. When heating some air-cooled engine pistons in an electric furnace, wholly stuck second rings could not be freed, even at 400° C., whilst the deposits from some top rings, which became free below 200° C., showed signs of melting. It is interesting to note that about 400° C. films of deposits on the upper surface of the ring groove started burning away and the deposits were rendered friable.

In air-cooled engine pistons generally the second ring is stuck in preference to the top and scraper rings. It is learnt¹¹ that this is also the usual experience in other laboratories. Of the specimens of liquid-cooled engine pistons examined, sticking of all the rings occurs.

Sticking on the slack side (or wherever the high temperatures might have been attained) is usual. In all cases of sticks substantial amount of carbonaceous deposit is present.

Close observation during the stripping of the rings from their grooves shows that the rings are not held in the groove by any "stickiness," but almost always by "wedging-in" of solid deposits between the upper surface of the ring and the top of the groove (especially where "hot sticks" are suspected), though sometimes they are also held in "moulds" of deposits in the back of the grooves (Fig. 11).

Further, the "wedging-in" of deposits over very small areas and in few places may hold the ring over 360° or at least over large areas. This is

especially true when the wedging is effected on either side of the ring gap.

The isolated areas of wedging may represent particular hot spots, *e.g.*, on the slack side. It is extremely difficult to remove the ring from these parts without breaking it into small sections and chiselling them out, whilst, when these sections have been removed, large sections of the rings can be freed without much effort and may even be deposit free.

Even in cases of complete "stick" when the rings have been stripped they have been found completely free of deposit on the underside and only a few marks of deposit on the upper surface; the rest of the surface may be quite clean and even polished. Thus no actual building up of deposit may occur on the upper surface of the ring unless the engine run has been prolonged after "hot stick." There is always a large amount of product in the grooves and, when the rings are stuck, patches of thick layers of deposits on the top of the groove.

Microscopic examination.

Examination under the microscope shows that the piston deposits are composed chiefly of fragments of coke-like bodies of various sizes and textures, containing varying proportions of oily, resinous, and asphaltic substances along with metallic wear products, and also dust particles introduced in the engine through the air intake. The asphaltic and resinous bodies act as binders or cementing medium for the coke-fragment fillers. When a large quantity of soluble matter is present, the deposit has a spongy appearance, a velvety lustre, and when etched with suitable solvents falls into minute fragments of coke (Figs. 1 & 2). With more highly carbonized types of deposits the coke fragments are comparatively large, and they undergo little change when treated with solvents except for removal of superficial oil.

The nature of the residual cokes after solvent treatment may differ very markedly from one another. The coke from a free top ring (when the second ring of the piston was stuck) had a greyish appearance with a steely and graphitic lustre. It was also densely packed, with a fine-grained texture, and was brittle and friable (Figs. 3 & 4).

The cokes from the stuck second and top rings generally show a different texture (Figs. 5 to 9), although some parts on disintegration may show textures similar to those from the free top ring groove. Under reflected light it has a dull non-lustrous appearance with porous or vesicular texture typical of products of low-temperature carbonization. Some show a layer effect due to carbonization of successive layers (Fig. 9).

The deposits from the lower rings and piston interior (Figs. 1 & 2) show that these are very small fragments of coke with some fine carbon and metallic dust particles bound together by soluble matter. The deposits on successive solution gradually break down into smaller particles, whereas the original samples as obtained by scraping from the stuck upper rings hardly ever disintegrate.

The difference in the texture of the cokes from free top and stuck second rings suggests that the deposits might have been altered or decomposed in different ways in the two ring-grooves.

In contrast to these are the deposits from the piston crown; these are

non-coherent, dense, and minute carbon particles or carbonized matter mixed with a large amount of metallic substances. Figs. 10 and 10A illustrate these.

Thus the appearance of the deposits according to their position indicates that temperature may have decisive influence on the initiation of ring-sticking.

Chemical Analysis of the Deposits.

The piston deposits are considered as asphaltic bitumen, mixed with highly carbonaceous substances, metallic wear and corrosion products, lead deposits from the fuel and siliceous matter from the air intake.

Little is known regarding the constitution of asphaltic bitumens, but they are now generally regarded as colloidal systems—blown asphalt may be regarded as a mixed isocolloid,¹² where the gel is composed of α units (soluble and freely rotating molecules), β units (soluble molecules fixed by secondary Van der Waal forces), and γ units (molecules fixed by means of primary valences) and are insoluble. Although for physical calculations α , β , and γ units may be considered as increasing polymerization and/or condensation products of simple monomers, the physical properties of the various fractions justify a further separation of the α , β , and γ fractions into several groups. This is the classical classification of asphaltic products into oils, maltenes, asphaltenes, carbenes, and carboids based on fractional solubility. In a system where molecules are held together largely by adsorptive forces, it is justifiable to classify the components on the basis of their solubility in solvents of increasing internal pressure, surface tension, polarity, etc.

Based on this fundamental principle the classification of the compounds of the piston deposits adopted follows:—

	Nature of the substance.	
1. Extracted with isopentane	Oils (includes also soft resins extractable by precipitation with liquid propane).	
2. Petroleum ether, 60/80° C. (aromatic free)	Maltenes or resins.	} Melting below 150° C.
3. Ethyl ether or ethyl alcohol	Highly oxygenated resins, asphaltenes;	
4. Carbon tetrachloride	solid, no apparent melting point when pure, but decomposes into semicoke with intumescence when heated above 300° C.	
5. Benzene		
6. Carbon disulphide	Carbene type of compounds—more condensed asphaltenes—which when heated neither swell nor decompose up to 500° C.	
7. "Carbon plus volatiles"	Insoluble in CS ₂ . Determined by ignition at 850° C.	

In our more recent work we have introduced chloroform, pyridine and pyridine plus carbon disulphide for further fractionation of piston deposits, but for the purpose of this paper the fractionation is confined to the six solvents named above.

The fractionation is carried out in successive stages with the solvents (in the order named) in porous (6–12 mu) bottom porcelain crucibles in large excess (25 : 1) of the solvent (analar quality) at room temperature. The preliminary precipitation of the fractions is carried out by allowing the solution to stand for a fixed period in the dark.

The metallic wear products are then extracted with 5N-HCl on steam

bath, washed with hot distilled water to remove the chlorides, and dried. The residue is ignited in an electric muffle furnace at 850° C. to obtain carbon plus volatiles and ash. The results are presented in Tables I and II on metal, ash and oil, metal and ash-free basis.

DISCUSSION OF THE RESULTS.

Carbonization.

From microscopic as well as chemical analyses it is evident that the greater part (69 to 85 per cent. or 93 to 99 per cent. on oil-free basis) of the ring-groove deposit of organic origin is composed of "carbon" or coke. If carbonization of the oil deterioration products in the ring's grooves is

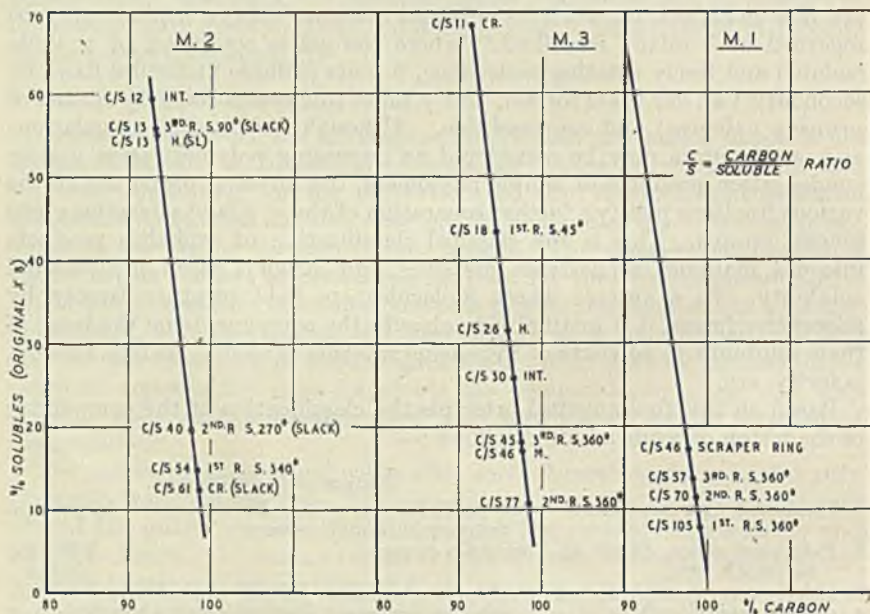


FIG. 12.

PISTON DEPOSIT ANALYSES ON *iso*-PENTANE SOLUBLES, METAL AND ASH-FREE BASIS (SEE TABLE II).

primarily a function of temperature, then the degree of carbonization should conform to the ring-belt temperatures, *i.e.*, should increase with higher temperature. This progressive relationship would be expected to be ideally shown by deposits from a piston where all the rings are completely stuck, so that the ratio of "carbon" to "solubles" cannot be upset by any fresh deposition.

That carbonization in the ring grooves is a function of temperature is indicated by Figs. 12 and 13, where the percentage of "carbon" has been plotted against solubles on *isopentane*-solubles free basis. Reference to the analytical data on Table I will explain any deviation from the rule. M. 1 presents nearly an ideal case. All the upper rings were completely stuck and carbonization was quite advanced. Even the *isopentane*

solubles ("oils") show perfect gradation in percentage (Table I). M. 2 provides another good example. The sample from the hollows was taken only from the slack side, where higher temperatures are probably attained. It is therefore not surprising that its position nearly coincides with that of the third ring which was stuck over a small area. This latter fact also accounts for the third ring being so removed from the second ring. M. 1 and M. 3 show that when the second and third rings are stuck the compositions of the deposits are not dissimilar (Fig. 12). In M. 3 the top ring contained a high proportion of isopentane soluble which was obviously freshly introduced as further evidence by the high proportion of solubles

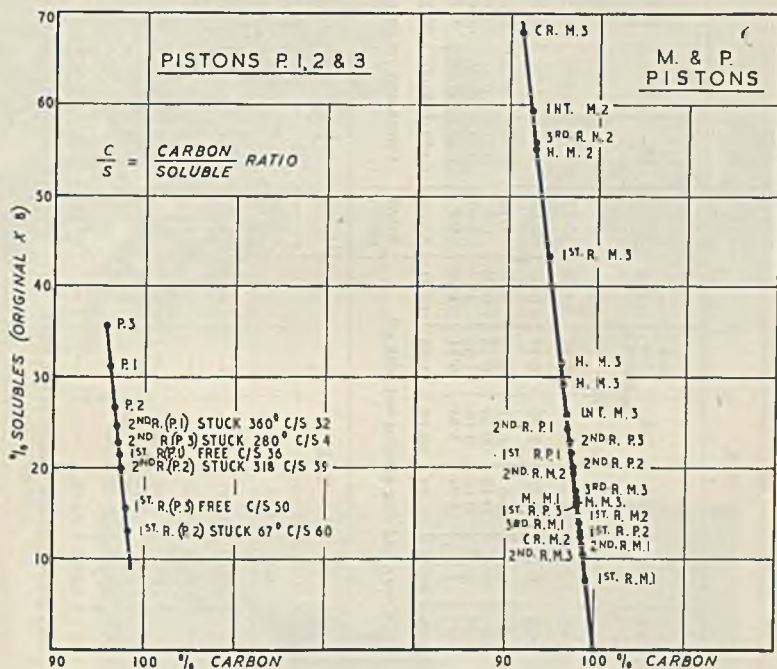


FIG. 13.

PISTON DEPOSIT ANALYSES ON 130-PENTANE SOLUBLES, METAL AND ASH-FREE BASIS (SEE TABLE II).

on the crown. Other pistons show that when the sticking of the top and second rings are comparable, or no fresh deposition has taken place on the top ring, the carbonization is always more advanced in the latter than in the second ring. Air-cooled engine test pistons also conform to this general rule.

In Fig. 13 analyses of all the samples from the two types of pistons are plotted together. This shows that the compositions of stuck upper rings (including the top ring, which may be partially stuck or free) both from the service as well as test pistons are very similar. It further suggests that at least 97 per cent. (on oil, metal, and ash-free basis) of the deposit is carbonized when the rings are stuck or the sticking is fairly advanced.

TABLE I.

Engine :	M. 1.				M. 2.						M. 3.							
Ring :	1st.	2nd.	3rd.	Mud-groove and scrapers.	Crown.	1st.	2nd.	3rd.	Hollows (slack).	In-terior.	Crown.	1st.	2nd.	3rd.	Mud-groove.	Hollows Duplicate Analyses.		In-terior.
isoPentane sol- ubles	14.02	16.40	20.17	33.33	33.02	14.50	12.00	14.18	23.32	26.73	30.77	26.46	15.30	18.10	22.50	24.32	24.20	20.36
Pet. ether sol- ubles	0.0	0.22	0.0	0.0	0.59	0.24	0.27	2.30	0.26	0.0	2.38	0.66	0.27	0.31	0.23	0.52	0.58	0.24
90% alcohol sol- ubles	0.47	0.14	0.03	0.13	0.0	0.0	0.0	0.81	0.82	2.53	1.70*	0.78*	0.15*	0.52*	1.03*	1.68*	1.70*	1.45*
CCl ₄ solubles	0.0	0.0	0.0	0.19	0.0	0.0	0.19	0.23	0.23	0.05	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₂ H ₆ solubles	0.0	0.15	0.30	0.10	0.70	0.32	0.65	1.02	1.51	1.14	1.01	0.33	0.21	0.21	0.02	0.23	0.20	0.0
CS ₂ solubles	0.34	1.40	1.02	0.00	0.40	1.0	1.05	1.63	2.51	1.74	0.0	2.12	0.46	0.72	0.35	0.42	0.48	0.90
Carbon and vola- tiles	85.17	81.60	78.48	65.20	64.30	83.85	85.85	79.83	71.35	67.81	55.05	60.65	83.61	70.33	75.81	72.83	72.84	77.05
Remarks . . .	Ring grooves dry.				Crown and ring grooves wet with oil.						Ethyl ether.	Crown and 1st ring groove wet with oil.					Others dry.	
Engine :	P. 1.				P. 2.						P. 3.							
Ring :	1st.	2nd.				1st.	2nd.					1st.	2nd.					
isoPentane insol- ubles	14.13	18.15	—	—	—	12.20	15.21	—	—	—	—	15.41	15.54	—	—	—	—	—
Pet. ether sol- ubles	0.51	0.18	—	—	—	0.23	0.25	—	—	—	—	0.15	0.13	—	—	—	—	—
90% alcohol sol- ubles	0.0	0.0	—	—	—	0.08	0.33	—	—	—	—	0.50	0.64	—	—	—	—	—
CCl ₄ solubles	0.0	0.0	—	—	—	0.0	0.12	—	—	—	—	0.0	0.0	—	—	—	—	—
C ₂ H ₆ solubles	—	—	—	—	—	0.0	0.22	—	—	—	—	0.22	0.41	—	—	—	—	—
CS ₂ solubles	1.82	2.30	—	—	—	1.12	1.23	—	—	—	—	0.72	1.22	—	—	—	—	—
Carbon ad vola- tiles	83.54	79.37	—	—	—	86.37	82.04	—	—	—	—	82.91	82.06	—	—	—	—	—
Remarks . . .	Dry grooves (piston washed in petrol).				Dry grooves (piston washed in pet. ether 60/80° C.).						Dry grooves (piston washed in pet. ether 60/80° C.).							

Deposit Analyses on Metal and Ash-free Basis.



FIG. 1. $\times 40$.



FIG. 2. $\times 40$.



FIG. 3. $\times 100$.

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FIG. 4. $\times 75$.



FIG. 5. $\times 50$.

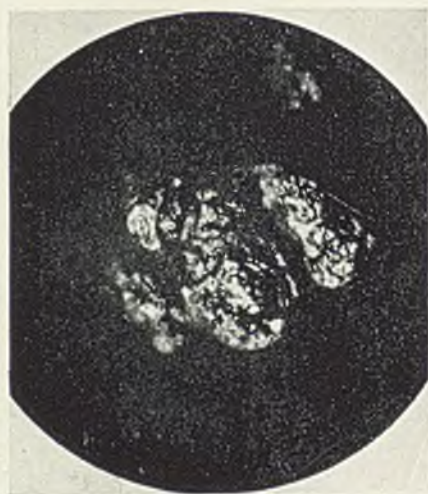


FIG. 6. $\times 50$.

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FIG. 7. $\times 40$.



FIG. 8. $\times 40$.

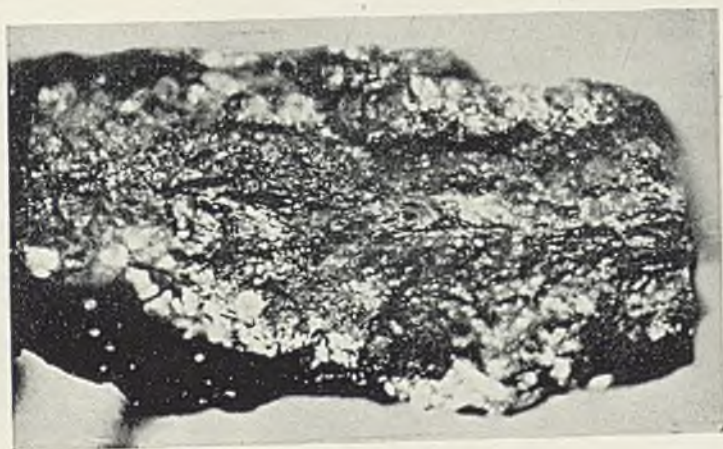


FIG. 9. $\times 40$.

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FIG. 10. $\times 40$.

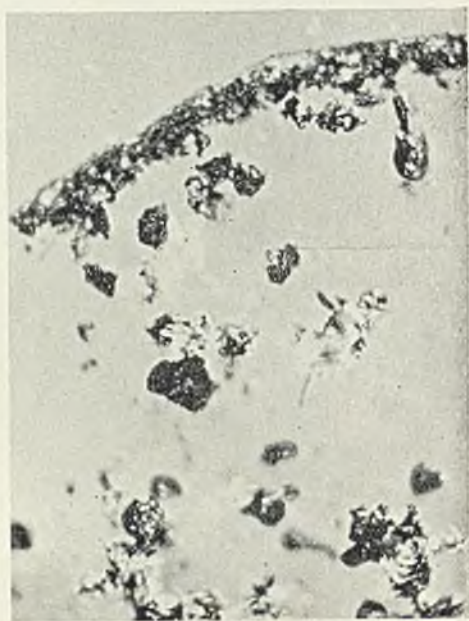


FIG. 10A. $\times 40$.



FIG. 11. $\times 10$.

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TABLE II.

Engine :	M. 2.				M. 2.						M. 3.							
Ring :	1st.	2nd.	3rd.	Mud-groove and scrapers.	Crown.	1st.	2nd.	3rd.	Hollows (slack).	In-terior.	Crown.	1st.	2nd.	3rd.	Mud-groove.	Hollows Duplicate Analyses.	In-terior.	
Pet. ether sol- ubles	0-0	0-26	0-0	0-0	0-80	0-28	0-31	2-08	0-34	0-0	3-05	0-90	0-32	0-38	0-30	0-67	0-77	0-30
90% alcohol sol- ubles	0-54	0-17	0-04	0-45	0-0	0-0	0-0	0-94	1-07	3-45	2-07*	1-06	0-18	0-64	1-33	2-16	2-24	1-82
CCl ₄ solubles	0-0	0-0	0-0	0-28	0-0	0-0	0-22	0-27	0-30	0-07	0-0	0-0	0-0	0-0	0-0	0-0	0-0	0-0
C ₂ H ₆ solubles	0-0	0-18	0-40	0-28	0-11	0-37	0-73	1-19	1-07	1-56	1-68	0-45	0-25	0-26	0-03	0-30	0-26	0-0
CS ₂ solubles	0-40	0-80	1-28	1-14	0-61	1-17	1-20	1-90	3-27	2-37	0-0	2-88	0-54	0-89	0-45	0-54	0-63	1-11
Carbon and vola- tiles	99-06	98-50	98-28	97-85	98-39	98-18	97-54	93-02	93-05	92-55	91-50	94-71	98-71	97-83	97-89	96-33	96-10	96-77
Ratio = $\frac{\text{Carbon}}{\text{Solubles}}$	105-38	60-85	57-14	45-51	61-11	53-85	30-65	13-32	13-38	12-42	10-76	17-9	76-52	45-08	46-39	26-25	24-9	20-90
Remarks	Stuck 360°	Stuck 360°	Stuck 360°	—	—	Stuck 180°, slack side.	Stuck 270°, mostly slack.	Stuck 90°, slack side.	—	—	Ethyl ether.	Stuck 45°, slack side.	Stuck 360°.	Stuck 360°.	—	—	—	—

Engine :	P. 1.				P. 2.						P. 3.							
Ring :	1st.	2nd.				1st.	2nd.					1st.	2nd.					
Pet. ether sol- ubles	0-59	0-22	—	—	—	0-26	0-30	—	—	—	—	0-17	0-16	—	—	—	—	—
90% alcohol sol- ubles	0-0	0-0	—	—	—	0-09	0-39	—	—	—	—	0-70	0-76	—	—	—	—	—
CCl ₄ solubles	0-0	0-0	—	—	—	0-0	0-14	—	—	—	—	0-0	0-0	—	—	—	—	—
C ₂ H ₆ solubles	—	—	—	—	—	0-0	0-26	—	—	—	—	0-26	0-49	—	—	—	—	—
CS ₂ solubles	2-12	2-81	—	—	—	1-28	1-45	—	—	—	—	0-85	1-45	—	—	—	—	—
Carbon and vola- tiles	97-29	96-97	—	—	—	98-37	97-47	—	—	—	—	98-02	97-14	—	—	—	—	—
Ratio = $\frac{\text{Carbon}}{\text{Solubles}}$	35-90	32-00	—	—	—	60-34	38-52	—	—	—	—	40-50	33-97	—	—	—	—	—
Remarks	Free.	Stuck 360°.	—	—	—	Stuck 67°.	Stuck 318°.	—	—	—	—	Free.	Stuck 280°.	—	—	—	—	—

Deposit Analyses on isoPentane-solubles, Metal and Ash-free Basis.

Carbon/Soluble or C/S ratio.

Although over 95 per cent. on oil-free basis of the deposit is carbonized when the rings are stuck, the converse is not generally true, the exceptions being the top rings, which may be stuck or free although C/S ratio (given in Table II) is nearly always higher. Under varying conditions of running (e.g., the Service pistons) naturally the C/S ratios are applicable for comparison only when the deposits from the same pistons are considered, but they are comparable when engine-running conditions are also comparable (e.g., the Test pistons). It will be seen that the C/S ratios of the second ring-groove deposits from the P. pistons lie between 33 and 39, whilst those from service engine deposits are generally higher, which is not surprising, as they have been subjected to longer runs.

There is a marked difference in C/S ratios of deposits from top and second rings, as well as of deposits from stuck and unstuck rings, the exceptions, again, being from top rings. This suggests a critical difference in conditions of ring-sticking between the top and second rings. If ring-sticking was purely a function of the degree of carbonization, then all rings with high C/S ratios should be stuck in preference to those having lower ratios.

Generally speaking, the production of soluble deterioration products of oil in the ring grooves is also a function of temperature, except when the critical conditions are involved.

R.A.C. Variation diagram.

The above considerations indicate that ring-sticking takes place under a set of critical conditions and that the "mode" of carbonization may be more important than the degree of carbonization. The only way to investigate this factor from the available data is to analyse the intermediate products of reaction, i.e., the solubles. For evident reasons the isopentane solubles cannot be used. The rest for general treatment have been divided into three major groups on the basis of physical properties. These are: Resins (R) the sum of petroleum ether and alcohol- or ethyl-ether-solubles; Asphaltenes (A) the sum of carbon tetrachloride- and benzene-solubles; and Carbon disulphide solubles (C). C indicates to an extent the intermediate stage of alteration beyond A. On oil and carbon-free basis $R + A + C$ is calculated to make up 100 and plotted on a triangular basis (Fig. 14).

It will be realized that the solubles are not directly proportional to the carbon content but are only intermediate products of carbonization. From theoretical considerations three possible relationships of the intermediate products may be shown by the diagram:

- (1) A linear relationship between the third, second, and top rings, the positions of the upper rings being farthest removed from the R-pole. The line may swing either towards A- or C-pole (Fig. 14), according to the conditions. This linear relation would exist if the conditions of carbonization were progressive and no critical factors intervened between the ring-belts.
- (2) A linear relationship as in (1), but the relative positions of the samples from the ring grooves will be reversed. This would be expected when the rings are all stuck or, due to stoppage of further

supply of oil, the composition of the deposits has remained virtually unchanged and the engine has been run for some time after these conditions are reached. Under such circumstances the temperature in the various belts may be higher than usual, but it is difficult to sort out this effect from that of "time." The advanced intermediate reaction products—*i.e.*, A and C—would be expected to diminish with higher temperature belts due to their comparative instability to thermal treatment.

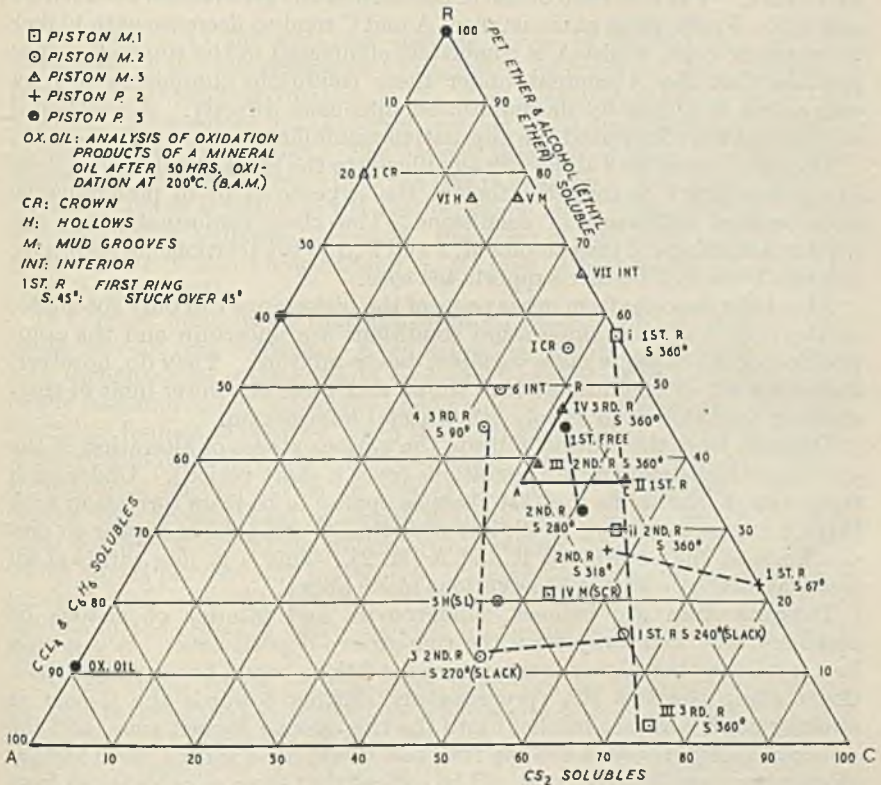


FIG. 14.

R.A.C. VARIATION DIAGRAM ($R + A + C = 100$). (ANALYSES PLOTTED ARE ON γ PENTANE SOLUBLES, CARBON, METAL AND ASH-FREE BASIS.)

(3) An angular relationship—*i.e.*, a combination of the vertical and horizontal relationships—between the samples from the rings (as shown by the lines RA and AC in the field of the diagram). This would be expected only when some critical factor—*e.g.*, temperature and/or oxidation—intervenes between the ring belts, for then the conversion of the earlier products to A or C may no longer be proportional.

Fig. 14 shows that only the second and third possibilities are fulfilled. The first condition applies only as long as the second and third rings are

considered, and then only as a part of condition (3). This again substantiates our previous deduction that although conditions in general may be progressive between the third and second rings, critical factors intervene between the top and the lower rings.

The second theoretical possibility is illustrated by the plottings from M. 1 supported by P. 3. It has been pointed out (Appn. II) that in M. 3 the deposits have either been subjected to unusually high temperature or exposed to usual temperatures over a prolonged period after all the rings were stuck. The C/S ratio of the deposits from the grooves are between 57 and 105. Under these circumstances A and C tend to decrease with higher temperature belts, whilst A is completely eliminated in the top ring. It is possible that the A content under these conditions diminishes not by conversion to C but by decomposition into coke directly. A horizontal shift would have indicated the alternative possibility.

The plottings of M. 3 almost ideally illustrate the third possibility. Here in the top ring C is formed either at the expense of or in preference to some critical difference in conditions. The close conformation of the inter-relationships of the samples M. 2 and P. 2 to the relationship shown by samples from M. 3 further supports the case.

About the deposits from other parts of the pistons one can only speculate, as the nature of the temperature conditions are uncertain and the composition of the deposits more variable, due to mixture. They do, however, indicate a set of conditions which shows that there is a lower limit of ring-sticking conditions and supply other useful information.

Deposits from the crowns indicate the various stages of alteration of the oils under high-temperature conditions (over a short period). Under such temperature conditions the first changes appear to be resin formation with little A compounds (*e.g.*, M. 3), but with time C compounds appear to predominate at the expense of R and A (M. 2). This is in line with known facts, as well as with the observations made above.

Deposits from the hollows, mudgrooves, and interior of pistons lie scattered, but well away from the ring-groove deposit zone. It can only be speculated that higher temperature conditions would have pushed them down along the line RA (progressively shifting towards the C-pole as sticking conditions are reached) into the ring-groove deposit zone, and the critical conditions round the top ring belt would have shifted them farther along a line parallel to AC. It will be noticed that some samples taken from the slack sides where higher temperature conditions might be expected do indicate that such transformations (hollows, M. 2; mud-groove and scraper M. 1) take place.

It will also be seen from the RAC diagram that deposits from M. 2 also lie well removed from the general convergence field of stuck second rings (as well as top rings). In this piston all the rings were only partly stuck, and the C/S ratios are fairly low compared to other M. deposits. The chief feature is the relative higher concentration of A. All other stuck second rings appear to have lower proportion of A (M. 2 perhaps provides an example of a boundary case between hot and cold sticks). As indicated before, this difference may be due to the fact that with hot sticking A decomposes (not converted into C, as the C content of all the second rings are quite comparable).

DISCUSSION (GENERAL).

The facts to be explained are :—

- (1) two types of sticking of rings : (a) " cold stick " and (b) " hot stick " (irreversible);
- (2) the preferential sticking of the second ring in both Service and test engines;
- (3) mechanism of ring-seizure.

In addition to the anti-ring sticking forces of detergency, peptizing properties of the oil, resistance to oxidation or cracking, etc., mechanical factors, of which ring rotation is the most powerful, must be taken into account. There does not, however, appear to be any definite or accurate information on the subject. The force of this movement is known to have sheared off a screw driven to hold the ring in position. An indirect evidence of this influence is found in the case of engine trials with polished (lapped) and unpolished (unlapped) rings.¹³ Polishing of the rings leads to faster sticking. It is also known that ring-sticking is hastened by holding the rings in position.¹³

It appears improbable that any resinous product of low melting point could prevent ring rotation. Even a gradual reduction of such products into carbonaceous matter would be ineffective against the scraping action of the ring movement unless the yield value of the material was very high. Complete fouling of the ring, when the engine is running, would be possible if the ring movement could once be stopped. This would require a kind of spontaneous decomposition or coking at one or more spots. If such coking were accompanied by strong swelling, then the conditions would be ideal for hot stick. This coking with swelling would provide a wedge which would prevent ring movement, after which seizing of the ring would proceed with mounting effect. The wedging coke must also be able to withstand the crushing action exerted by the up-and-down movement of the rings.

In the initial stages of deposition there can be imagined a constant struggle between the anti-ring sticking forces and deposition of the alteration products. The outcome of this struggle would chiefly depend on the rheological behaviour of the products. If the products behaved as true viscous systems in an oily medium, the rate of deposition would be small. If, on the other hand, plastic conditions prevailed, the rate of deposition (and coking of the deposited products) would be increased enormously. Production of a large amount of asphaltenic substances would confer such plasticity, which would also at the same time raise the melting point of the deposit. This production of plasticity and a high yield value would be favoured if the resinous substances were insufficient or incapable of peptizing or dispersing the asphaltenes (due to loss of peptizing properties). If the forces due to ring movement were negligible, then this alone could effect ring-sticking (cold). Production of more insoluble bodies—*e.g.*, CS₂ solubles in preference to asphaltenes—would deprive the deposit of the binding medium, and hence allow erosion of the deposits by ring rotation.

Chemical evidence suggests that a maximum amount of asphaltenes (CCl_4 and C_6H_6 solubles) is produced in the second ring grooves. The asphaltenes mixed with resinous matter act as a "binder" of the insoluble organic and inorganic bodies. At a suitable temperature and under non-oxidizing conditions these asphaltic products may decompose into "coke" and gas. This coking may be accompanied by strong swelling. Figs. 5 and 6 show deposits of this nature before and after heating. Such asphaltic products are known to decompose into coke when heated above 300°C . accompanied by swelling.^{14, 15, 16} Due to the permeating nature of the binder, the carbonized asphaltene particles (which are known to sinter together on coking) would form a bridgework structure which would reinforce the insoluble part of the deposit, much as steel nets reinforce cement concrete. This would impart a "shatter strength," or a capacity to withstand impact, to the deposit. Thus the resulting coke would be ideal to produce a "hot stick." Such coking may start at one or more hot spots or over a certain area of the upper surface of the ring groove. From all considerations, this type of carbonization appears to be favoured by the second ring-belt conditions. In the top ring grooves the formation of CCl_4 and C_6H_6 soluble type of asphalt products are either not favoured or they are fast converted into CS_2 soluble and insoluble type of products, which on carbonization appear to yield brittle and non-agglutinating types of "carbon." These latter types of compounds, which may not essentially differ from the more soluble asphaltic products, are known to form at temperatures round $360\text{--}70^\circ\text{C}$.¹⁷ Their formation from asphaltenes is highly accelerated by oxidation conditions,¹⁸ and they neither melt nor swell. It is possible that such temperature and oxidation conditions prevail generally in the top ring-grooves and are the cause of frequent freedom from sticking of the top ring, when the lower rings are stuck. As the combustion gases directly impinge on the top ring, there would also be accelerated erosion of the carbonaceous deposits from the ring-grooves.

The composition of the deposits preceding initiation of "hot sticks" may be favourable to produce "cold sticks." If the temperature conditions remain below the decomposition point of the asphaltenic products, very prolonged running would perhaps be required to produce any appreciable sticking. The condition could be ignored from the service point of view were it not for the fact that a sudden burst of more drastic conditions would convert it into a hot stick.

RHEOLOGICAL CONSIDERATIONS.

Many theories have been advanced to account for the mechanism of oxidation of hydrocarbons, but whichever theory be accepted, oxidation of mineral oils at low or moderately high temperatures is undoubtedly accompanied by the formation of unsaturated compounds, which, by further oxidation, condensation or polymerization, may give rise to resinous and asphaltic substances. At higher temperatures the products of oxidation may be more liable to decomposition than to further oxidation.

The thermal instability of hydrocarbons with increasing molecular weight is a well-established fact. Oxidation of hydrocarbon mixtures proceeds

spontaneously with the formation of resinous bodies. Further oxidation condensation accompanied by mild cracking would give rise to asphaltic products. The conditions for the formation of these resinous and asphaltic products are more favourable on the cylinder wall and in the ring-grooves than in the crankcase, although the reactions may have been initiated in the latter. Cracking of thermal decomposition of hydrogen mixtures also yields unsaturated bodies, mono- and di-olefins (which polymerize to resinous bodies), and aromatics. The latter, according to their nature, by splitting and condensation produce progressively higher-molecular-weight compounds, and end up as coke-like products.

The long-chain alkyl aromatics are substituted in the manner of paraffinic chains, and are more stable than polycyclic aromatics which yield higher-molecular-weight compounds more readily. The more unsaturated type of condensed ring systems polymerize directly and readily. The first stage of cracking of all condensed compounds appears to be towards more condensed systems poorer in hydrogen.¹⁹ If therefore such substances liable to form an adherent and swollen coke by thermal decomposition are formed from mineral oils, then any lubricant would cause ring-sticking under suitable conditions. The criterion to rate the ring-sticking tendency of oils under given conditions would therefore be which oil would *produce more and deposit more* of these substances in the ring-groove in a given time? Only a physical property which reflects the composition of deteriorated oil and its colloidal behaviour can be a guide towards the answer of this question. Such a property is obviously the rheological properties of the deteriorated oil under given conditions. There is need of greater knowledge of the temperature and atmosphere conditions of the engine itself.

Little is known about the actual chemical constitutions of these components of asphaltic systems, but the balance of evidence shows that asphaltenes are probably a combination of units comprising cyclic groups of no more than two or three rings condensed together. Gruse,¹⁹ summing up the evidence, concludes that they are "built up of repeated simpler units strung together, much as amino acids are assembled into proteins." There is little doubt, however, about the colloidal structure of asphalts.

It is now generally considered that the constituents of asphaltic bitumens are in various states and degrees of mutual colloidal dispersion. The asphaltenes are lyophobic with respect to aromatics, terpenes, chlorinated hydrocarbons, and carbon disulphide, but lyophobic towards paraffins and naphthenes and are coagulated by them.²⁰

Nellensteyn^{21,22} considered the asphaltic system to be composed of:

- (i) a medium;
- (ii) a lyophile part (consisting of protective colloids);
- (iii) a lyophobe part (consisting of asphaltene micelles).

If the last two be considered as a dispersed phase, then evidently the stability and the flow behaviour of the system are governed by the relation between the micelles and the medium. According to Nellensteyn, the most important factor affecting the stability is interfacial tension.

Pfieber and Van Doormal¹⁵ suggest that the system consists of asphaltenes dispersed in the "maltenes," the former being predominantly

aromatic or hydroaromatic in character. His experiments, supported by later work in the B.P.M. laboratories, clearly show that the dispersing medium or the maltenes govern the rheological properties of the system.

They showed that if the maltenes are highly aromatic (or hydroaromatic) in nature, the asphaltenes are so well peptized that the resulting system may flow readily and behave as a truly viscous fluid. Maltenes of slightly lower peptizing power give rise to products which have a plastic character. If the peptizing properties are still further lowered, by removal of aromatics by oxidation, or if the maltenes are themselves transformed, by condensation or heating, then the system would have a very strongly plastic character. The importance of these phenomena shown by bituminous products in the ring grooves in relation to ring-sticking will be readily appreciated. A rheological method of approach to evaluate ring-sticking tendencies of oils at high temperatures is therefore indicated. Such investigations are now in hand, and have already produced some interesting results, which will be published in due course.

CONCLUSIONS.

Ring-sticking appears to result from the following causes. The altered, probably oxidized, oil enters the ring-grooves with successive strokes of the piston. Prolonged exposure, which may be needed to alter them further to asphaltic substances, is only possible in the shelter of the ring-grooves. There, carbonization of small portions of the successive deposition products proceeds, causing the layer effect in the coke seen under the microscope (see Fig. 9) until the deposit has been built up, but the ring remains just free, due to scraping action exerted by ring movement. The process of building up the deposit would chiefly depend on the *rate of deposition in the grooves*, which is a function of the *flow properties* of the system composed of "thickened oil and deterioration product" under the conditions in the grooves.

Under a set of optimum and critical conditions a maximum amount of asphaltic products are formed in the ring-grooves which decompose into coke. The carbonization may take place through the production of more insoluble types of asphaltic products—*e.g.*, by condensation—when the resulting carbon is brittle and is capable of neither wedging the rings nor withstanding any crushing. Under non-oxidizing conditions, carbonization may take place by coking, similar to destructive distillation of the asphaltenes.

This coking may be accompanied by swelling, where the conditions are ideal for hot stick. Such coking need not take place over a wide area, but may occur at isolated areas representing "hot spots" due to blowby, etc. Once the hot stick is initiated, it is a matter of time before which the rings would be completely held. The latter process appears to be especially favoured by the second ring conditions in the air-cooled S/C engines. The critical condition deciding the nature of carbonization, which may decide whether a ring would be irreversibly held, may be temperature and oxidation or temperature alone. Thus cold and hot sticks may be attributed to the thermoplastic and thermosetting properties of the resinous bodies

produced by oil deterioration. In the latter case thermosetting resin of the asphaltene type, on heating, become infusible, and above a critical temperature decompose into a coke accompanied by swelling. The swollen hard coke wedges in the ring in its groove, after which ring-sticking occurs at an accelerated rate. The mechanism of coking is much the same, as in the formation of semi-coke or coke from bituminous coals during low-temperature carbonization.

APPENDIX

*The Condition of the Pistons from which the Samples were Collected,
Together with the Particulars about Ring-sticking.*

M represents liquid-cooled service engine pistons and P represents air-cooled test engine pistons.

Position of sample.	Ring-sticking.	General remarks.
M. 1.		
Top ring	Stuck over 360°: strongly held on the slack side, but easy to remove from thrust side. Ring gap on sl. side.	Heavy coating of scaly and fused deposit on the slack side but only smooth lacquering on thrust side and no sign of fused deposit. The broken part of 3rd ring sunk in the groove and coated over with deposit. Ring grooves dry and free of oil. The rings held in "mould" in the back of the groove as well as "wedged-in" between the ceiling of the grooves and the upper surface of the rings. Hours of run: unknown. Oil: unknown.
2nd ring	Stuck over 360° otherwise as in top ring.	
3rd ring	Stuck over 360°. Otherwise as in top ring. Broken 1 in. from the ring gap.	
Top scraper and mud groove	Scraper missing 240°, 120° remaining stuck. Deposit from md. gr. collected with ring deposit.	
M. 2.		
Crown	Thick deposit. Soaked with oil.	Probably a specimen representing setting in of sticking conditions. The rings were all held in the groove. Actual wedging only on the slack side. 3rd ring probably a cold stick, easy to remove. Scrapers missing. No deposits in the grooves. Mud groove coated with deposit. All rings wet with oil.
Top ring	Stuck over 240° on sl. side, 20° broken and missing on thrust side.	
2nd ring	Stuck over 270°. One end 90° on thrust side free.	
3rd ring	Only 120° present. 90° of this stuck on sl. side.	
Hollows: Sl. side only	Thick deposit. Dry.	
Interior	Thick deposit. Fairly dry.	

APPENDIX—continued.

Position of sample.	Ring-sticking.	General remarks.
M. 3.		
Crown	Thick dull deposit. Wet with oil.	Piston in fairly good condition. Deposit from top ring had a shiny pitch-like appearance on the stuck part. In other parts dense brittle deposit typical of top ring. Probably a cold stick. 2nd and 3rd rings were strongly wedged and had to be removed by chiselling inch by inch. Scraper rings also held but little deposit. Running conditions: unknown. Oil: unknown.
Top ring	Stuck over 45°. Ring gap on thrust side.	
2nd ring	Stuck over 360°. Ring gap on sl. side	
3rd ring	Stuck 360°. Ring gap on sl. side. Broken $\frac{1}{4}$ in. near gap.	
Top scraper and mud groove	Scraper held over 270°. Sample mixed with deposit from mud gr. immediately below. Easily freed.	
Hollow: Both sides	Thick deposit on slack side but less on thrust side.	
Interior	Dry, thick deposit.	
P. 1: R.A.E. S/C tests.		
Top ring	Free.	Hard brittle deposit in top ring. Hard flaky carbon on crown. Scraper free. Oil: S. 100; Batch 101; Duration of test: 50 hours.
2nd ring	Stuck over 360°.	
P. 2.		
Top ring	Stuck over 67°.	Grey thin crust of carbon on crown. Black lacquering all over piston. Oil: R.D.E./0/94. Run: 50 hrs.
2nd ring	Stuck over 318°.	
P. 3.		
Top ring	Free hard brittle deposit.	Patches of brownish-black lacquer on both sides. General condition good. Oil: R.D.E./0/70. Run: 50 hrs.
2nd ring	Stuck over 280°.	

The P pistons were superficially cleaned with petroleum ether before the deposits were collected.

In the majority of pistons stripped for examination, whenever the rings were completely sealed in, the ring-gaps were found to be situated on the slack side.

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CHEMISTRY DIVISION,
ROYAL AIRCRAFT ESTABLISHMENT.

THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute of Petroleum was held at 26 Portland Place, London, W. 1, on Wednesday, November 14, 1945, when a paper entitled "Investigation of Piston-Ring Sticking in High-Duty Aero-engines," by Dr. A. Lahiri and F/Lt. E. Mikolajewski [see pp. 59-77], was presented and discussed.

THE PRESIDENT (Professor F. H. Garner), who occupied the Chair, said: This paper was sent to the Institute some time ago, and was referred to by Dr. Lahiri in the Viscosity Symposium. Until to-day we have not had the opportunity to fit the paper into our programme; but it is of such interest that we feel that it should be presented so that an opportunity is afforded for discussion.

In the absence of Dr. Lahiri, the paper was read by F/Lt. Mikolajewski.

DISCUSSION.

THE PRESIDENT (Prof. F. H. Garner) said he found the paper particularly interesting because of the viewpoint from which its subject was presented. The phenomenon of ring sticking in aero-engines which the authors had been considering had to be co-related with two other known types of ring-sticking which had also been met during the war period. One was the ring-sticking which was found in diesel engines; it was experienced when making investigations of the quality of diesel fuel for the Services to give satisfactory operation at low temperatures. It was found that fuels of low cetene number at low temperatures did give rise to cold ring-sticking but, on warming up, the engines operated satisfactorily. That type of phenomenon was tied up with the formation of formaldehyde in the exhaust gases, and one wondered whether the formaldehyde might not play some part in forming resins present with asphaltenes in the ring grooves.

The other type of ring-sticking which showed those cold and hot characteristics was that which occurred when a small amount of such a product as glycol or glycerol leaked into the engine, as, for example, in liquid cooled aero-engines. He thought most people concerned with these matters were familiar with that type of sticking, and there must be some chemical explanation. The piston might become stuck in the cylinder, and when cold, in some cases it could not be forced out without destroying the piston when cold; but warming up would ease it.

MR. E. A. EVANS said that without having had time to study the paper it would be grossly unfair to attempt any criticism. But there seemed to be a postulate permeating the paper which assumed the formation of coke. It appeared that "coke" in this paper definitely meant carbon, as a chemist understood it, and nothing else; but no proof of its composition was given. It was quite possible, and indeed probable, that the chromatography which was proceeding in authors' laboratory would reveal more accurately what the

material was. He had been for many years doubtful whether any coke was formed in these deposits. The only evidence produced in the paper was microscopic. He could not believe that microscopical examination would reveal sufficient evidence that the material was coke. There was an assumption that when the asphaltic bodies were heated to a temperature of 300° C they swelled and produced coke. He did not remember sufficient of the details of the papers which were quoted in the bibliography, but would say that he did not think there was proof in those papers that the material was really carbon. He thought such assumptions should continue to be challenged until someone proved that the material was carbon.

Frankly, he had no idea how to estimate pure carbon in these deposits. Time would show whether chromatography would solve the difficulty. He was quite sure that the solvents mentioned in the paper would not do it. For a number of years he had extracted deposits with all the solvents which the United States had been able to ship to England—and they were many—but he had never been able to get anything which approached pure carbon. The oxygen content of the deposit had been always high. After selective extracts, the oxygen content of the residues had increased up to as much as 35 per cent. He could not imagine that, with 35 per cent of combined oxygen, the material could be called coke or carbon.

He felt that many authors of papers had taken a risk in the past in making a similar assumption, rather than providing sufficiently accurate means of ascertaining whether or not the material was pure carbon. He imagined that physical methods would prove valuable.

F/Lt. MIKOLAJEWSKI, agreeing with Mr. Evans, said that from the purely chemical point of view the word "carbon" meant carbon which could be separated from its associated substances as a pure element. In common language it did not mean pure carbon, and the authors realized that the substance with which they were concerned in the paper was not pure carbon; it contained some other substances soluble in a powerful solvent, such as pyridine. They found that the separation of this deposit would not have been helpful in arriving at an explanation of the ring sticking. With chromatographic methods, even after pyridine extraction, and after extraction by the use of a solvent as strong as hot hydrochloric acid, the substance which was left from the piston deposit was not pure carbon, but still contained something difficult to estimate under their conditions. There was carbon and highly carbonaceous compounds the nature of which he did not know at the moment.

MR. EVANS suggested that the mistake should not have been made in the paper of calling something carbon which was not carbon; he thought it was just perpetuating an error which had led to so much confusion, and suggested that it should be stated somewhere that where "carbon" was mentioned it meant something else.

THE PRESIDENT felt that Mr. Evans was perfectly consistent. The first paper of his published in the *Journal of Institution of Petroleum Technologists* in 1921 was entitled "The Carbonization of Lubricating Oils," and in it reference was made to the "Conradson carbon content." Dr. Ormandy, who presented the paper, changed the word "carbon" to "coke" through-

out, and he thought that Mr. Evans made more or less the same comment at that time.

MR. EVANS said he did.

DR. D. CLAYTON said he was rather surprised to see it stated that when the rings were made smoother they would stick more readily. He had thought it was the other way round—that the rougher the rings were the more readily they would stick by reason of the adhering carbon.

His other point related to pegging the rings. It was unfortunate that this should have the effect of accelerating ring-sticking, because he understood that pegging was a good way of securing quick running in, particularly in view of the in and out movement of the cylinder walls due to flexibility.

F/Lt. MIKOLAJEWSKI said that as to the sticking of the rings which had a polished surface, his view was that there was catalytic action, and this should be borne in mind. But the subject was very complex and, not knowing the exact conditions, or rather, unless one did know the exact conditions of the particular engines under discussion, one could talk for hours and would still find difficulty in arriving at a proper conclusion.

MR. H. L. WEST thought the authors were a little unfortunate in having chosen to present a paper on a subject so controversial, and he was going to continue where Mr. Evans had left off. He considered the whole subject had been made very abstruse by the continual references to asphalt; so far as he knew, there was no evidence to show that the deposits occurring in engines had any relation at all to asphalt. The authors referred continually to asphaltenes, but we did not know whether the asphaltenes were the same as the substances which occur in asphalts. He had a strong suspicion that they were nothing like them. His impression, from an examination of quite a lot of the deposits, was that most of the asphaltenes were metallic compounds of acidic organic material of definitely complex structure. We had to find out how they arose. The President had mentioned that in diesel engines there were aldehydes formed in the combustion; it could not be said that that was not so also in the gasoline engine, because there was aldehydic combustion even on compression; a cold flame reaction took place on the compression stroke before the charge was fired. Further, in all engines there was continuous blow-by past the pistons. Therefore, it must be expected that the products of partial combustion would possibly be found in the ring grooves, as well as any oil that got there. If aldehydes were there, thermal polymerization could be expected.

He thought the authors had gone rather too far, and that in examining deposits only from stuck rings it would have been better to have examined the deposits further down the piston and to have tried to find out what happened to those deposits when they are heated.

The great difficulty in this business was to find out exactly where those deposits came from. He suggested that time might usefully be spent in running one of those engines on hydrogen, making sure that the temperature conditions are the same as when running on gasoline, and ascertaining what sort of deposits were found and whether there was ring-sticking. Until that was done he did not think there would be much advance towards the solution

of this problem. It was known that in an automobile or an aero-engine so-called "carbon" was formed from the combustion. The blow-by was bound to introduce that into the ring groove; and if the deposits lower down the piston, or long before ring-sticking had occurred, were examined it would usually be found that they contained an extremely finely divided "carbon" in quite large proportions. If, instead of using the normal solvents, the authors cared to go further and use, say, very dilute alkali, it was quite likely that they could separate it. It was probably the compressive action of the ring which formed the very hard carbonaceous type of deposit.

When he heard that the R.A.E. were to tackle this problem he had hoped that there would have been a completely new approach to the subject. It was unfortunate, however, that they had merely proceeded along the lines followed by others during the last 20 or 30 years. It was up to them now really to show the oil companies how to do the job.

F/Lt. MIKOLAJEWSKI said their observations had been concerned with aero-engines only. They had compared the piston deposit with the products obtained after the extraction of natural asphalts; when using the same type of solvents, and in the same range, it had been found that the separated components had similar properties. They had also used the chromatographic method, which enabled the substances to be obtained in the pure condition. The work had not yet been published, and he had not identified the substances; but he had made some estimations and comparisons on the basis of the molecular weights of the separate substances. He had not the data with him, but would like the opportunity to present it at some time. But they had the basis on which to judge between the two types of products, and had noted their similarity.

He expected that in both cases there were some metallo-organic compounds, but had no evidence yet that this was so or of what kind they were. The work was continuing and he hoped that in the future he would be able to give some data about the kind of substances which he had separated from the piston deposits. He had collected 175, and expected to increase the number to 200.

MR. J. D. F. WEST said that it seemed that nearly always it was the second piston ring which stuck, rather than the top ring. F/Lt. Mikolajewski had hinted that the conditions in the second ring groove must be very different from the conditions in the top ring groove, and he wondered whether those differences were temperature differences, and if so, whether any data could be put forward with regard to the relative temperatures in the top and second ring grooves.

F/Lt. MIKOLAJEWSKI said it was a very common observation, not only at the R.A.E. laboratories, but also in others, that the second ring would stick, while the top ring remained free. The authors thought the explanation was that the sticking of the piston occurs where critical temperatures arise and where the deposit decomposed and swelled at the time the ring is wedged in the groove. Knowing that the temperatures in the top rings were higher than in the lower rings, it is judged that the top rings are more likely to stick than the lower rings. But at the higher temperatures the vibration of the engine could be helpful in disintegrating the deposit, which is believed

to be brittle at higher temperatures, and therefore removing it. It was this he felt that helped to keep the top ring free; but he would not be definite about it until there had been a much closer examination, not only of the deposit, but also of the working conditions of the engine. It was appreciated that it was very difficult to ensure that engines were working under exactly similar conditions at any one time.

MR. G. H. LEE questioned the accuracy of the statement that the lower rings stuck more readily than the top rings, at any rate in the case of the air-cooled engine. Maybe it was a little dangerous to generalize in respect of the air-cooled engine; but in the single-cylinder sleeve valve engine the results were different. That might be due to some effect of heat flow; there might be a distribution of engine temperature peculiar to that engine.

F/Lt. MIKOLAJEWSKI said they had dealt only with the Merlin and Pegasus engines, and he could not speak about the pistons of other types of engine.

MR. D. L. SAMUEL said he also had made analyses of a large number of deposits over a great many years and had tried to correlate the analyses of the deposits with the condition of the rings; he had worked through a large range of solvents, but could not say that he had effected that correlation. But in the course of the work he did make the very interesting discovery that a large amount of oil-free deposit from the engine was soluble in aqueous caustic soda. In some cases even as much as 30 to 40 per cent of the deposit could be removed by extracting with aqueous alkali; and when this solution was acidified it precipitated a dark gelatinous substance. He had not had the opportunity to go further in this investigation, but in some respects this precipitate had a superficial resemblance to the humic acid which could be extracted from coal.

He thought the authors and other who carry out this type of work had a very difficult task in finding out the reason for piston-ring sticking and trying to correlate the condition of the deposit with the condition of the engine.

Another factor which might have to be taken into consideration was the effect of additives, several of which would delay ring-sticking, but might not prevent it. Perhaps if it was known how they worked some ideas would be gained on sticking. He could not believe that temperature was everything and had seen a number of ring-sticking experiments in which a small motor cycle engine was run at a cylinder temperature such that the top ring would stick in 5 hours; by incorporating additives the cylinder temperature could be raised by very many degrees. If it was the effect of temperature that caused ring-sticking, one would think that, with the increase of temperature, ring-sticking would still occur in spite of the presence of the additives, since there would doubtless be a sufficiency of deterioration products to fill the ring grooves. Moreover, with some additives temperatures might have to be raised over 50° C. to obtain sticking during this short term test.

A study of the mode of action of these additives would contribute largely to our knowledge of the causes of ring sticking.

F/Lt. MIKOLAJEWSKI said the additives would in many cases delay ring-sticking because they acted at first as anti-oxidants. There were many

others which were called anti-corrosive additives. But it did not follow that they completely prevented the sticking of piston rings; the sticking could still occur after a longer period of working under the same conditions. When using different kinds of oil it was observed that in some cases the sticking occurred early and in other cases later. By studying temperatures it had been found that at all performances of the engine the temperature must be a very important factor influencing the stickiness; but before the critical temperature was reached it was possible that the rheological properties of the deposit coagulated between the ring and the groove were important. It depended on whether the deposit was becoming plastic or whether it was in the flowing condition. For that reason, the physical properties of the products in the ring groove, as they were affected by the chemical changes, were factors that must be borne in mind.

MR. G. H. THORNLEY referred to the recent paper in the *S.A.E. Journal* by Denison and Clayton on ring sticking. It was well known that a large part of the deposit in the ring groove was acidic, and those authors suggest that there were oxy acids formed, by the oxidation of the oil under certain conditions, which are soluble in the oil only to the extent of about 0.2 per cent. Beyond that figure they were precipitated, and at a temperature of 500° F. or above they polymerize into very resinous sticky bodies which they consider were largely responsible for ring sticking. From that basis they work up an explanation of the behaviour of metallic anti-ring-sticking additives, suggesting that the oxy acids displace the original acid from the metallic soap, forming a metallic "oxy-acidate" which is soluble in the oil and is therefore washed away; and the original acid, chloro-stearic acid perhaps, also goes into solution.

At the same time, the effect of combustion products, the peroxides, aldehydes, and so on must not be forgotten.

MR. R. A. FRASER said that reference had been made to the effect of aldehydes and the formation of metallic soaps, but nobody had mentioned the possibility of nitrogen entering into sludge formation. One of the troubles in connection with the supply of coal gas in the past had been the formation of gummy material, which was traced to the reaction of nitric oxide and unsaturated hydrocarbons in the gases. It would be interesting to know whether the authors had found any nitrogen in the sludges to which they refer.

Another point was that he thought the Germans used nitrous oxide for boosting their aircraft engines at high altitudes. Was there any evidence that such a procedure resulted in increased ring sticking? He thought that oxides of nitrogen might play a part in the formation of sludges.

F/Lt. MIKOLAJEWSKI could not reply definitely at the moment, but hoped to be able to do so later when he had separated the piston deposit components. He was awaiting facilities to identify those compounds.

DR. W. E. J. BROOM said that about fifteen years ago, just about the time when he joined the company with which he was now associated, the question of nitrogen peroxide in sludges was first observed. He did not know whether or not a great deal of attention had been paid to the matter, although it

had been known for a long time. The speakers that evening had been criticising the authors rather strongly, and while he would have liked to have taken up the cudgels on their behalf, he was afraid he could not.

He was somewhat disappointed that no reference was made in the paper to fuel. His own belief was that what happens with a given oil in a given engine could not be dissociated from the particular fuel in use. With a different fuel the balance might be altered so that there might or might not be ring sticking.

He did not think there was such a thing as carbon. The ordinary so-called carbons, he thought, were hydrocarbons, where the carbon/hydrogen ratio was very high. Even if one tried to make these carbons as carbons, his experience was that one had to graphitise the structure before one could get rid of the hydrogen and oxygen. If carbons were prepared from natural sources, such as coconut shell or by the carbonization of coal, it was impossible to get out all the ash. It might not matter very much whether the substance to which the authors refer as carbon was really carbon, or coke, or coal; and in fairness it should be remembered that the word "carbon" was in inverted commas, which seemed to indicate that the authors did not really think it was carbon in the sense that Mr. Evans referred to it. A substance which could carbonize in the same way as bituminous coal would presumably fit their argument.

He was going to ask how the authors accounted for the action of detergent type additives. F/Lt. Mikolajewski, in one of his replies, had suggested that the anti-oxidant part of the additive was perhaps important for delaying the onset of ring sticking. If that was what he intended to convey, he (Dr. Broom) disagreed with it and did not think that was the answer. Equally, however, he could not suggest what the answer was.

Finally, he suggested that the ultimate aim of this work should be to indicate how to select an oil without going to the trouble of a long and unreasonably expensive engine test, because he thought it doubtful whether some of the small engine tests really could give the true answer. A quick test was wanted to determine whether any particular oil would stick the piston rings in a given engine using a given fuel.

F/Lt. MIKOLAJEWSKI said that no mention of the influence of fuel could be made without having examined the whole process of combustion; they had no data about it in respect of the Service engines. As to whether the fuel or the oil was responsible for sticking, it seems to him that the fuel was not lubricating the piston; therefore, he thought the simplest answer was that the oil was responsible for the stickiness.

DR. B. PUGH said the paper did not contain any evidence to justify the statement that there are two types of ring-sticking, (i) cold sticking and (ii) hot sticking, which were stated to be irreversible.

To an engineer the term "hot stick" meant purely and solely a stick while the engine was running, and a "cold stick" meant that the ring groove when hot contained insufficient depth of deposit to prevent ring movement; but after the piston had cooled down and had been removed from the engine, the side clearance between ring and groove was decreased due to differential contraction, and in this reduced space the deposit was sufficient in depth to hold the ring securely. Obviously, then, if after the

state of affairs had been reached where, if the engine was then shut down, the rings would be completely cold stuck, running was continued *under the same conditions*, the built-up of deposit would continue, and not cease, as the authors presumably supposed, until the rings were held with engine still running—i.e., a "hot stick" was obtained.

A "hot stick" was not fundamentally different from a "cold stick," and was only irreversible because the deposit in the ring groove had accumulated sufficiently to prevent the ring functioning at the working temperature of the piston. A "cold stick" might with continued running develop into a "hot stick" *under the same operating conditions*. That process did not necessarily require the more drastic conditions postulated by the authors. Consequently, to give the impression that "cold sticks" could be ignored was altogether wrong.

The authors quote results from deposits scraped from pistons which had run on D.T.D. 472 type oil tests at the R.A.E. In these tests, to simplify and standardize the procedure, oils were classified according to the amount of cold sticking obtained after a standard running time. In this way oils were rated or classified in a manner which was generally confirmed in service. This state of affairs could not have prevailed if cold sticking were of no significance.

The difficulty in freeing "hot stuck" rings in the laboratory could be explained when the method of detecting hot sticking was understood. The method commonly used was to shut down when excessive fog issued from the breather. This excessive fog would be due to hot products of combustion passing the stuck rings. Some time would elapse before sufficient fog had accumulated in the crankcase and had made itself evident at the breather. During this time the rings, already held by deposit more or less filling the clearance space of the ring grooves, would be subjected to temperatures well above their working temperature and well above the 300° C. quoted as the critical temperature by the authors, especially at local points. At these temperatures the ring groove clearance spaces would be practically full of deposit, and the rate of deposition of products from both the fuel and oil would increase rapidly. It was not to be wondered that, when the engine was ultimately shut down, the rings were wedged in place, and that when the piston was heated in the laboratory to 300° C. the rings were still held. This definitely applied to the cases of "hot sticking" reported at the R.A.E. during the rating of oils. Consequently, there appeared to be no justification for the authors' assertion that "hot sticking" was fundamentally different from "cold sticking."

A factor of importance was the mechanical strength of groove deposits, subject as they were to compression, abrasion, erosion and shear.

Conclusions drawn from the examination of pistons from service should be accepted with reserve. Although such deposits were useful for the development of analytical technique, generally nothing was known as to the conditions—e.g., engine temperature, mixing strength, oil used, etc.—under which the deposits were formed. It was difficult to see how any definite and final conclusions could be arrived at unless running conditions were carefully controlled. For example, the authors mentioned the composition of deposits from crowns of pistons without any reference to running conditions. Obviously, if the mixture were rich, much of the carbon would

be from the fuel, together with approximately 50 per cent lead. Analyses of ring-groove deposits should be based on deposits obtained from the grooves up to the time that "ring-gumming" commenced—*i.e.*, when an "incipient stick" was obtained, under controlled conditions.

That sticking of the top ring during D.T.D. 472 tests was unusual was due to the fact that in many cases excessive groove wear was experienced. He had discussed this point more fully elsewhere.* Briefly, ring groove wear appeared to be due to the oil used, piston-ring surface finish, condition of piston material, piston clearance, piston proportions, and location of the ring concerned. The top ring side clearance, which before test was standardized at 0.006 in, after test reached a maximum of 0.023 in, depending on the oil used. Sticking of the top ring was experienced with 6 per cent of the oils tested.

Decreased ring groove wear was probably the explanation of why, as a previous speaker had mentioned, sticking of the top ring was more common in the Hercules engine.

F/Lt. MIKALOEWSKY said their evidence for the existence of "cold and hot stick" was detailed in the paper. The points raised by Mr. Pugh were discussed in the same argument. Though there might not be a fundamental difference between "cold stick" and "hot stick," it could not be denied that their had always been a fundamental difference between the points of view of engineer and the chemist, and cold logic was often superseded by hot argument.

MR. H. L. WEST thought the remarks of Dr. Broom illustrated how easy it was to become tied up in terminology. He started by referring to the fact that effect of the fuel could not be neglected, and then wanted to know which oil stuck the rings. He (Mr. West) did not think that, in order to arrive at a working hypothesis of the action of the additives, or even of the oil, one had to form a picture in their mind of what was happening. A line he had been working on for some time was that there was a tendency for the combustion product to accumulate in the ring grooves. His view—and it seemed to be borne out to some extent by practice—was that the oil acted by virtue of the fact that it washed out the material that got into the ring groove and sent it down to the sump. Once the stage was reached where it could no longer do that, ring-sticking was almost bound to occur. It was known that the additives which gave the best anti-ring-sticking performance held in suspension the carbonaceous matter in the oil and did not allow it to deposit around the engine. That view might not be the best, but it was certainly one way of looking at the matter.

To continue with the nitrogen story, he asked what about the bromine in the fuel? There was no reason why there should not be some of that in the deposit. He had found evidence of bromine compounds in the ring grooves, but how it got there he did not know.

Engine deposits were tricky things to work with. If a deposit had been once taken into solution in solvent and allowed to dry, it might not be possible to take it up again with the same solvent. He suggested the

* "Papers on Piston Ring Problems," read before the Institution of Mechanical Engineers, November 30, 1945.

authors should be extremely careful in the chromatographic work, because they might alter the extracts they were using while they were working with them.

F/Lt. MIKOLAJEWSKI asked whether Mr. West had done chromatographic work?

MR. WEST replied in the affirmative.

F/Lt. MIKOLAJEWSKI then asked whether he had prepared his substance in the dry conditions for this work?

MR. WEST said he had not done a lot.

F/Lt. MIKOLAJEWSKI said that in this case he was not keeping the deposit in the dry state after extraction. He kept it in solution, and changed the solvent for every chromatograph. He evaporated *in vacuo* to a certain degree, and there should be some solvent left in. But in other cases, after complete evaporation, he observed the same result as Mr. West, that the substance was only partially soluble.

MR. J. H. PIGNÉGUÉ suggested that there were not, fundamentally, two types of sticking of piston rings as suggested by the authors, but that it was merely a matter of degree. He suggested that what was referred to as a "cold stick" was really part way to a "hot stick."

The preferential sticking of the top ring might usually be explained by the fact that the top ring and groove were subject to greater wear than the second.

Regarding the point that polished rings stick more readily than unpolished ones, his experience was that an unpolished ring in early life lost some of its width due to removal of its relatively rough surface. This removal produced a certain amount of abrasive material, which also helped to keep the ring free. These two effects were sufficient, at any rate over a test period of a few hours, to keep the ring free. These effects were largely absent with a polished ring, and therefore sticking occurred more readily.

THE PRESIDENT said he was sure all would be anxious to congratulate F/Lt. Mikolajewski on the way in which he had replied to the discussion. He was sure also that they would look forward to further papers from the Royal Aircraft Establishment on the subject of piston-ring sticking. On all the occasions on which papers have been presented to the Institute on "carbonisation" of lubricating oils, whether in piston rings or elsewhere in engines, the audiences had always been critical and would, he hoped, continue to be so. He hoped, however, that authors of papers would not be discouraged.

(The vote of thanks was accorded with acclamation, and the meeting closed).

MR. D. L. SAMUEL, in a written contribution, said: "In the opening sentence of their paper the authors state that 'While the severity of the conditions to which an aero-engine lubricant is exposed has increased manifold with the increasing power output of aero-engines in recent years, no parallel development in the production of lubricants which can stand up to such drastic conditions has yet taken place.'

"I cannot altogether agree with this statement, since the modern high duty aero-engine will now operate for about 300 to 350 hours without major overhauls on present straight mineral lubricating oil, while some of the lower output engines will operate for as long as 1,200 hours without overhaul. When it is realized that 300 hours operation may correspond to something between 50,000 and 100,000 miles, I think it will be obvious that the lubricating oil is fully capable of fulfilling the demands made on it in such engines."

In reply to Mr. Samuel F/Lt. Mikolajewski wrote: "Is it not more probable that engines are being designed to stand up to the lubricating oils which are produced rather than that oils are being designed to fit all engine conditions. Though the number of hours between overhauls is as stated by Mr. Samuel, there are instances where only 70 hours operation occur before overhaul is necessary. This fact is evidence that all is not what it might be as regards lubricant."

MR. S. E. A. MOON wrote: "During the discussion following the paper the authors received more criticism than appraisal. Like Dr. Broom, I should like to take up cudgels on their behalf, but, unlike this latter speaker, I feel able to do this in one important respect. I do feel that the basic property of the piston deposits on which the authors base their ring-sticking theory is substantiated by certain other well established evidence. I refer to the possible formation of a swollen, adherent coke leading to 'wedging' of the piston ring. It is well known that the coking property of certain coals is greatly reduced after extraction with benzene, in line with the suggestion that benzene-soluble containing deposits do form adherent coke. It is interesting to note that there is no evidence to suggest, however, that bitumen or asphaltic materials are responsible for the coking propensity incorporation of such materials in non-coking coals having no effect in this direction.

"After much investigation it has been concluded that resinous material, derived from plant spores, are the major cause of 'coking,' and it is further known that such resins are often present in coal as metallic derivatives. I suggest, therefore, that deposits containing metallic/organic derivatives are formed in service condition and may, on carbonization, or, to coin a term possibly more acceptable to Mr. Evans' and others' terminology, coke-ification, lead to a swollen coke of high 'shatter strength' and consequent ring-sticking.

"A possible explanation of the mechanism of 'additives' presents itself here. As is well known, carbonaceous resins, having the ion-exchanging properties of natural zeolites, can be extracted from coals by the action of sulphuric acid. These resins, in the form of their metallic derivatives, can then be made to base exchange with any other organo/metallic constituents of the piston deposits, being of a similar resinous nature, will base exchange with the metal additive, introducing into the resin a metal which would not lead to the same injurious effect. The organic derivatives of lead, barium, zinc, etc., for instance, would not be expected to impart the same strengthening lattice effect to a coke as, say, iron or aluminium. It would be interesting to ascertain whether metals derived from the additive are concentrated in the benzene-soluble portions of the deposit, or metals of

the piston lining are retained as soluble components in the bulk of the oil. It is worth noting that ion-exchanging resins similar to those prepared from coal have been recently synthesized by condensation of unsaturated aliphatics with formaldehyde.

“I might add that recent investigation carried out by myself has shown that metal derivatives of oxy-acids of hydrocarbons have a marked affinity for nitrogen, a property not shown to a similar extent by the free oxy-acid.”

F/Lt. MIKALOJEWSKI, wrote : “I was very interested in Mr. Moon's contribution. It confirms our points of view on the similarity of the products obtained in ring-sticking deposits, and from blown asphalts. We have found that in our alcohol extract of ring deposits, there are some organo-lead compounds, but we do not yet know their chemical nature.”

MECHANISM OF ACTION OF ORGANIC CHLORINE AND SULPHUR COMPOUNDS IN EXTREME-PRESSURE LUBRICATION.*

By C. F. PRUTTON, DAVID TURNBULL, and GEORGE DLOUHY.

INTRODUCTION.

Mechanism of Frictional Forces between Metal Surfaces.

Lubricants serve to prevent damage to metal surfaces slid-over one another and to reduce the frictional force between them. In order to formulate mechanisms for various types of lubrication, it is necessary to consider the nature of frictional forces between two metal surfaces. After the discovery by Amontons¹ in 1699 that frictional force is independent of apparent surface contact area and for specified materials proportional only to the force normal to the contact area, it was assumed that frictional force represented the force necessary to pull the load over the surface protuberances from one interlocking position to another. This theory, which was advocated by Coulomb² and others, satisfactorily explained Amontons' law and other known phenomena connected with friction, and was widely accepted for 150 years after Amontons' discovery. Recently Bikerman³ has reviewed and defended this viewpoint on the origin of friction.

Adhesion Theory. Although accepting the theory of friction just mentioned, Coulomb and other early investigators recognized the possibility that frictional forces might have their origin in the adhesion or welding together of solids at their points of contact. Investigations made in recent years have lent very strong support to the theory that frictional forces are exerted principally to overcome adhesion rather than to overcome interlocking of surface asperities. Evidence for this point of view has been furnished by the high dependence of frictional forces upon the composition of thin films between the sliding surfaces. In the absence of any films other than of air, the coefficient of friction is generally less than unity, and of the same order of magnitude for a wide variety of substances. However, Bowden and Hughes⁴ point out that when the adsorbed air film normally coating solid surfaces is removed from metals by degassing *in vacuo*, the coefficient of friction rises to very high values, and in the case of gold reaches 30. On the other hand, Rayleigh⁵ and Hardy⁶ have shown that a very thin film of certain substances, such as fatty acids, may greatly reduce the coefficient of friction. Proponents of the theory that friction is due to surface asperities had pictured lubrication as a process of filling up surface irregularities with the lubricant, which thus prevented the protuberances on the sliding surface from interpenetrating.

This theory was rather difficult to reconcile with the findings of Rayleigh,⁵ Hardy,⁶ and others that thin films of fatty acids reduce the friction

* From the Laboratories of Case School of Applied Science and the Lubri-Zo Corporation.

to a much greater extent than liquid films of hydrocarbons or water. Since the fatty acid molecules are not large enough to fill up the depressions, Devaux⁷ showed that the amount of fatty acid necessary to provide effective lubrication might be no greater than that required to form a monomolecular layer on the surface. These observations are easily explained upon the assumption that friction is caused by adhesion between high points of contact. While actual welding may have occurred at many of these points, the metals may be separated at most of the other contact points by oxide layers or by adsorbed gas molecules. When adsorbed gas films are removed by degassing *in vacuo*, the number of contact points at which welding has occurred is greatly increased and the coefficient of friction becomes very large. Fatty acids apparently reduce friction by strong adsorption on metal surfaces, including the contact points, thus keeping the metals from coming together and welding.

Adhesion Theory and Amontons' Law. If adhesion is to be accepted as the principal cause of friction, it must offer a satisfactory explanation for Amontons' law. When solid surfaces touch under a light load, contact is probably made at very few points. As the load is increased, deformation of the metal at the contact points occurs due to the increased pressure. The areas of the contact points are thus increased, and further contact may now be made at additional protuberances, which did not contact at the lighter loads. Due to the increased area of contact, a force greater by an amount proportional to the increase in contact area will have to be applied in order to overcome friction. Thus, if the actual point contact area is proportional to the load, a rational explanation of Amontons' law is offered. Analysis of the relation between loading and contact area has been made by Bowden and Tabor.⁸ If elastic deformation was assumed, it was shown that the contact area should be proportional to the two-thirds power of the load. When plastic deformation was assumed, it followed that the contact area increased proportionally to the load and the law of Amontons was thus explained. However, a difficulty arises here, in that if the metal is permanently deformed by a heavy load, the frictional force should remain the same when the load is decreased. Such is not the case, however, for, as heavy loads are decreased, the frictional force decreases in accordance with Amontons' law. An explanation for this may be found in the probability that only a slight motion or vibration in the solid bodies concomitant with the measurement of friction will slightly displace the bodies, so that an entirely new set of contacts is made.

Temperatures at Contact Points of Sliding Metals. Recently Bowden and his collaborators have carried out a series of investigations on the nature of sliding friction which have served to clarify greatly the concepts of this process, offering some of the most direct evidence available in favour of the adhesion mechanism. Rather high local temperatures are to be expected at contact points when one metal surface slides over another. In 1936 Bowden and Ridler⁹ reported experiments which gave fairly direct information on the magnitude of temperatures at these contact points during the sliding. Their method consisted in measuring the thermal E.M.F. produced at the contact points when a metal cylinder was made to slide over the surface of a dissimilar metal with an Einthoven galvanometer of very low period. For a constantan slider on an unlubricated steel surface,

temperatures as high as 1000° C. were recorded. Even with lubricant present rather high temperatures were found. Thus, using mineral oil containing Castrol X a temperature of 600° C. was reached, while with oleic acid a temperature of 320° C. was attained. Whenever a low melting metal was used as one of the surfaces, a temperature corresponding to the melting point of this metal was reached, and was not exceeded with a further increase in the load. Loadings used in these experiments were comparatively small and of the order of 5 kg/sq. cm. of apparent area.

Real Area of Contact between Metal Surfaces. Also of great importance was the work of Bowden and Tabor⁸ on the real area of contact between metal surfaces and its variation with load. Electrical conductivities were measured between spherical and flat metal surfaces. These were used to estimate the magnitude of the real area of contact. For surfaces of different materials under a given load the conductivities were in nearly the same ratios as the bulk conductivities. For any given material, the variation of conductivity with load approximated more closely that predicted on the basis of plastic deformation than on the basis of elastic deformation. These results are in agreement with requirements of Amontons' law. As would be expected, the conductivity for a given load was independent of the surface roughness and the apparent area of contact. Estimates were made of the ratio of the real contact area to the macroscopic contact area in a number of cases. For a load of 20 kg on an apparent surface area of 21 sq. cm. this ratio was 1 : 10,000, while for a load of 300 kg it had increased to 1 : 130.

Motion of Metal Moving Over a Metal Surface. Analysis of the motion of a metal moving on another metal surface in opposition to frictional forces was made by Bowden and Leben.¹⁰ Photomicrographs of the path of metal spheres moving on flat surfaces showed that the motion was discontinuous, and took place in a series of jerks wherein the slider stuck momentarily and then rapidly slipped to a new position, where it again stuck ("stick-slip" motion). When a hard metal slides on a soft metal it tears a track in the softer metal, and the real contact area as deduced by conductivity measurements varies in phase with the stick-slip motion, falling to a minimum during the slip. When a soft slider slips over a hard surface, the hard surface is undeformed, while a smear of the softer metal is formed on its path.

For similar metals the friction is much higher, and large fluctuations are observed in it. A large track is torn out of the flat surface, while the value of the real contact area is much higher than for dissimilar metals, and does not change so markedly during the motion. No correlation was observed between discontinuities of motion and surface roughness, for the same type of motion was obtained whether the surfaces were rough or very highly polished. When the surfaces were lubricated with mineral oil the motion was still of the stick-slip type, but when fatty acid was used as a lubricant the motion became continuous. These rapid fluctuations in frictional force during motion, accompanied by the tearing out of pieces of metal and permanent deformation of the surfaces, favour the conclusion that welding has actually occurred during the "stick," and that these welded contacts are broken, often with the result that small pieces of metal are torn out of the surface during the "slip."

Some Objections to the Adhesion Theory. Although the adhesion theory appears to explain most of the observed frictional phenomena satisfactorily, some difficulties remain. Among the most serious of these are: the failure of the frictional force to remain large upon the removal of heavy loads, which has already been discussed; and the dependence of frictional force upon surface roughness at comparatively low loads. On the basis of the adhesion theory the contact area should be the same irrespective of the surface roughness. Bikerman³ has recently criticized the adhesion theory on the basis of these and other objections, and has attempted to explain frictional phenomena on the basis of the roughness theory. Actually the two mechanisms are not mutually exclusive; and it may be that, at comparatively low loadings, surface interlocking is an important contributing factor to friction, particularly for very rough surfaces. At comparatively high loadings and high speeds, however, the work of Bowden and others would seem to indicate that adhesion is the main contributing factor to friction.

Mechanism of "Boundary" Lubrication.

Lubricants reduce the frictional force between metal surfaces either by interposing a fluid film of low shear strength between the surfaces, which keeps them from contacting each other, or by forming a film of low shear strength by chemical action or physical adsorption on the contact points which prevents the metals from welding at these points. Hydrodynamic or "thick-film" lubrication is the designation of the first type of action, while the term "boundary" lubrication is used to denote the second type. Hydrodynamic lubrication may be attained when the pressures between the bearing surfaces are not high. In this case a complete liquid film may be maintained between the surfaces, and the only shearing resistance will be that due to the viscosity of the lubricant film. When high pressures are exerted on the bearing faces, however, it will no longer be possible to maintain a continuous film, and lubrication under these conditions must be effected by films formed on the contact points by physical or chemical interaction between the metal and oil. Mineral oil itself is unable to undergo such an interaction with the metal surface, and in order for it to function as a boundary lubricant agents capable of bringing about such an interaction must be added.

Among the first of such agents to be employed were fatty acids. It has already been pointed out that amounts of fatty acid required are no greater than necessary to form monomolecular films on the metal surface. Bowden and Ridler⁹ found much lower temperatures were produced at the contact points of sliding metal surfaces for lubricants containing oleic acid than for untreated lubricants. Bowden and Leben¹⁰ found also that with lubricants containing fatty acids the stick-slip type of motion tended to disappear, and the slip of one metal surface over another became continuous. Boundary lubrication by fatty acids is probably effected by formation of an adsorbed film of acid on the contact points of sufficient strength to withstand the pressure tending to squeeze molecules out from between the contact points. Presumably preferential adsorption takes place whereby the carboxyl group sticks to the metal surface by dipolar interaction. To shear the film between these contact points, it is then only necessary to

exert a force sufficient to overcome the Van der Waals' interaction between the alkyl groups extending up from the contacting faces. It might be inferred that any molecule containing a polar group capable of interacting with a metal surface or of being strongly adsorbed on such a surface would serve to reduce friction under intermediate loads. Metal soaps, esters, ketones, and other compounds serve under these intermediate loading conditions with some degree of effectiveness. Much larger amounts of the latter types of compounds are required than of fatty acids to obtain equivalent lubricating effectiveness.

Lubrication under Extremely High Loads. As the pressure on the contact points becomes larger and the contact temperature increases, there is a lesser tendency for any adsorbed film to remain stable. At temperatures of 600–1000° C. there is little likelihood that even a monomolecular film of fatty acid would remain on the contact surface. Not only would the strength of adsorption be much smaller, but at these temperatures the acids would undergo thermal decomposition. It is therefore necessary under these conditions to form a film of low shear strength which is more stable. This is the function of "extreme-pressure" additives in hypoid lubricants which must form films of low shear strength capable of withstanding temperatures produced by very high tooth pressures. As was pointed out by Bowden and Tabor,⁸ "extreme-temperature" lubricants might be a more appropriate name for this type of lubricant, since the pressure per unit area on the actual points of contact presumably does not change with loading. It is the high temperatures developed by these loads which make lubrication of this character necessary.

Since most organic molecules are likely to be desorbed or decomposed under the conditions prevailing on the contact points of gear teeth, it is probable that most additives used in the lubrication of hypoid gears function by forming an inorganic film of comparatively low melting points or shear strength at the contact points.

There is considerable evidence in the literature which indicates that friction between inorganic films is often considerably lower than that between metals. Hughes and Whittington^{10a} have reported data comparing the coefficient of friction between copper surfaces and the same surfaces covered by various inorganic films which showed in all cases that the films reduced the friction by a substantial amount.

Mechanism of Action of Lead Soap-Sulphur Hypoid Lubricant. One of the first extreme-pressure additives for use in gear lubricants, which found widespread commercial use, was a mixture of sulphurized fatty oil and a lead soap. An improved form of this type of additive, which in general consists of an active sulphur compound and a lead soap, became particularly important with the advent of hypoid gears. It was assumed that this lubricant caused inorganic films to form between the gear surfaces, but the nature of the films is rather obscure. Perhaps the most direct information about the films formed by this type of lubricant was furnished by the electron diffraction investigations of Simard, Russell, and Nelson¹¹ in 1941. These investigators made electron diffraction studies of steel samples which had been subjected to the action of sulphur, lead naphthenate hypoid lubricants in laboratory static tests, in the S.A.E. extreme-pressure lubricant testing machine, and in actual service.

In static tests samples were heated in oils at 150° C. for various periods. Electron diffraction examination of the films formed indicated that lead sulphate was formed on the surface in the early stages of the reaction, while lead sulphide became apparent in the surface after longer treatment. An invisible unidentified film was formed when a sample of steel was heated in lead naphthenate stock containing no sulphur. However, samples treated in this manner showed lead sulphate after heating in oil containing only free sulphur. From this it was inferred that the mechanism of film formation involved initial adsorption of lead naphthenate upon the metal surface, which was followed by reaction of adsorbed lead naphthenate with the sulphur to form lead sulphate or lead sulphide. Films formed on the S.A.E. machine were similar in character to those formed in the static tests. Lead sulphide was formed much more readily at the higher temperatures in the static tests and at the higher loadings in the friction tests. Examination of gear-teeth after service tests using the hypoid lubricant showed an unidentified film which gave the same pattern, however, as that produced by partly reduced galena. It was inferred that this film might have been a lead-rich phase of lead sulphide. In view of this, and since the more drastic laboratory tests favoured formation of lead sulphide, it appears that under service conditions the action of a lead naphthenate-sulphur lubricant involves reaction of sulphur with adsorbed lead naphthenate to form the observed film.

Whether the film which is formed reduces friction by virtue of a low shear strength of the solid phase, or by melting under the conditions prevalent at the contact points, is not known. Simard, Russell, and Nelson¹¹ point out that FeS and PbS form a eutectic at 970° which is several hundred degrees below the melting point of iron. However, it is also known from the work of Tammann and Dahl¹² that lead sulphide becomes quite plastic at 700° under pressure, and presumably its shear strength under these conditions would be low as well.

Lubrication by Formation of Low-Melting-Point Compounds. Instances in which a comparatively low-melting eutectic provides the boundary film are believed by Beeck and co-workers¹³ to be furnished by organic phosphorus compounds. It was found by means of a four-ball lubricant testing apparatus of the type designed by Boerlage and Block¹⁴ that when mechanical wear was plotted against per cent of tricresyl phosphate added to the oil, the wear decreased up to a concentration of 1.5 per cent of the additive beyond which it increased. When gold-plated balls were used in place of steel in the machine, the amount of wear was unaffected by the additive. This latter observation suggested that tricresyl phosphate reduced wear by a chemical rather than a physical mode of action. At concentrations below 1.5 per cent the additive apparently reduced wear by forming a film by chemical interaction which reduced friction, and thus prevented mechanical abrasion. As the concentration of additive was increased, however, chemical interaction became more rapid and corrosion losses became as important as losses due to mechanical abrasion, hence the upturn in the wear *v.* per cent additive curve. Most effective in reducing wear was an oil containing both tricresyl phosphate and oleic acid. Beeck and co-workers¹³ explain the manner of action of this combination as a smoothing off of the high points of contact by chemical interaction between the phosphate and steel,

leading to a higher effective area of contact between the sliding surfaces. With the real contact area thus increased, temperatures at the contact points would be lowered, and oleic acid might therefore become adsorbed and lower the friction. Without a fatty acid the phosphate lubricant would be ineffective, since it is probably incapable of interacting chemically with the surface at comparatively low temperatures.

Beecik *et al*¹³ believe that the film formed on the surface by the action of phosphorus compounds on metals is a phosphide. In support of this it was found that iron phosphide was produced when iron, carbon, and tricresyl phosphate were heated together at high temperatures. Since the system iron and phosphorus exhibits a eutectic at a phosphorus concentration of 10 per cent at 1020° C., which is 515° C. below the melting point of iron, these authors propose that the film present when the metal surfaces shear is a liquid eutectic mixture of iron and phosphorus. Support for this conclusion is offered by the polishing action of these additives.

Chlorine-Sulphur Extreme-Pressure Additives.

Recently Davey¹⁵ has published tests on the effectiveness of various chlorine and sulphur compounds in reducing friction and wear in the "Shell" four-ball apparatus. He concludes that the function of a chlorine additive is to react with the iron at the contact points forming a readily sheared film of iron chloride. Chlorine additives in which the chlorine is attached to aliphatic carbon atoms gave lower wear and friction than those in which the chlorine is attached to an aromatic nucleus. This led to the conclusion that additives containing "labile" chlorine function more effectively as extreme-pressure additives. Of the compounds investigated, benzo-trichloride, benzyl chloride, and carbon tetrachloride, in the order named, were most effective in reducing wear and friction. Less effective were such materials as chlorinated paraffin wax, chloroform, and ethylene dichloride. From this, Davey concluded that the greater wear permitted by these compounds in his laboratory tests was due to reaction of iron with HCl which split out. Actually some of the compounds preferred by Davey, such as benzotrichloride, do liberate HCl freely under service conditions as shown by tests reported later in this paper.

Davey¹⁵ has shown that the extreme-pressure properties of active sulphur additives are due to the formation of an iron sulphide film. As evidence supporting this viewpoint, he obtained friction-time curves for an oil containing sulphur using the four-ball machine with steel balls originally uncoated, which were very similar to the curves obtained using an untreated oil with balls initially coated with a thin, uniform layer of iron sulphide.

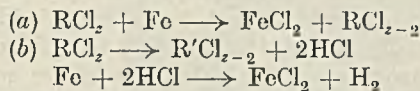
Although organic chlorine and sulphur compounds have been used singly as extreme-pressure additives, a lubricant containing both types of compounds gives more satisfactory performance under high-speed shock conditions than a lubricant containing either singly at comparable concentrations.¹⁸

For the past ten years a majority of all hypoid axles have been lubricated with mineral-oil lubricants containing both sulphur and chlorine compounds. This long record of successful service, confirmed by shock-test data,¹⁸ indicates that this type of lubricant is particularly effective in

hypoid lubrication. A thorough examination of the mechanism by which it performs its lubricating function is therefore warranted. It is the purpose of this paper to present the results of a study of the interaction with iron of chlorine and sulphur additives in oil solution singly and together, and to discuss the mechanism of gear lubrication by these additives in the light of the experimental results.

Possible Modes of Interaction of Chlorine Additives with Iron.

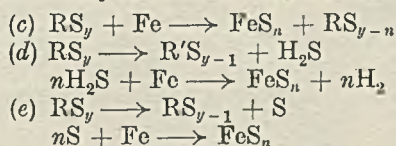
The following were considered as the most plausible modes of interaction of chlorine additives with iron :



In mechanism (b) it is possible for hydrogen chloride to split out by homogeneous decomposition of the additive in solution or by dehydrohalogenation catalyzed by ferrous chloride.

Possible Modes of Interaction of Sulphur Additives with Iron.

When sulphur or sulphur additives react with iron, sulphides having the general formula FeS_{1+x} , where x varies from 0 to 0.15, may be formed under certain conditions, in addition to the normally expected FeS^{16} . In the subsequent discussion we shall use the formula FeS_n (where $n = 1 + x$) in representing the reaction products between active sulphur additive and iron. Sulphur additives may then react with iron in the following ways :



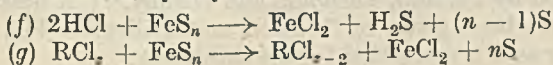
Here again decomposition of the sulphur additive into sulphur or hydrogen sulphide may be either a homogeneous reaction or one that is surface-catalyzed by iron or iron sulphide.

Possible Modes of Interaction of Sulphur and Chlorine Additive with Iron.

Co-operation between sulphur and chlorine additives may occur in a number of ways. It appears that the co-operation must lead to the rapid formation of a lubricant film presumed to be ferrous chloride, iron sulphide, or some mixture of the two. If ferrous chloride is considered to be the lubricant, sulphur compounds may favour its formation in one or more of the following ways :

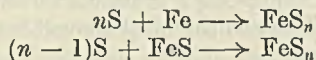
(1) Decomposition of the chlorine compounds into active products may be catalyzed by the sulphur additive or products formed therefrom, such as iron sulphide, sulphur, or hydrogen sulphide;

(2) Formation of ferrous chloride may be hastened if the chlorine additive or hydrogen chloride reacts more rapidly with iron sulphide than with iron itself, by any one of the following reactions :



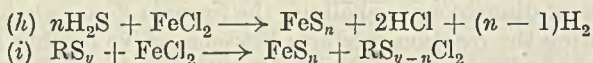
Sulphur formed in reaction (g) may have one or more of the following destinations :

- (g₁) dissolve in the oil phase;
- (g₂) react with either the chlorine additive or oil hydrocarbon to form a sulphide;
- (g₃) remain physically entrained in the film;
- (g₄) react with iron or iron sulphide as follows :



These mechanisms presuppose that the sulphur additive alone in oil forms FeS_n more rapidly at high temperatures than ferrous chloride would be formed by the reaction of the chlorine additive with iron. If iron sulphide is considered to be the lubricant, chlorine compounds might favour its formation in the following ways :

- (1) Decomposition of sulphur additive may be catalyzed by chlorine additive, hydrogen chloride, or ferrous chloride;
- (2) If the sulphur additive or its decomposition product reacted more rapidly with ferrous chloride than with iron, a catalytic action of chlorine additives on iron sulphide formation would be expected. This may take place as follows :



Also to be considered is the possibility that a film containing both iron sulphide and ferrous chloride may have better lubricating qualities than either ferrous chloride or iron sulphide. This might be explained by such a film having a low melting point or very low shear strength.

EXPERIMENTAL.

In order to establish which of the outlined mechanisms of the action of chlorine and sulphur additives are operative in gear lubrication, the following types of experiments were made : (1) " shock " testing of automotive gears, lubricated by the additive solutions, in a Chevrolet car ; (2) analyses of gear-teeth surfaces and lubricants for sulphides and chlorides ; (3) analysis for the decomposition products of the additives when hydrogen, hydrogen chloride, or hydrogen sulphide was passed through oil solutions of the additives ; (4) analysis of the product of chemical attack of the additive solutions on iron powder in the temperature range 150-250° C. ; (5) equilibrium studies of the system FeCl₂-FeS_n-H₂S-HCl ; (6) determination of rates of formation of ferrous chloride films in HCl, iron sulphide films in H₂S, and ferrous chloride-iron sulphide films in HCl-H₂S mixtures ; (7) melting points in the system ferrous chloride-iron sulphide.

Equilibrium studies of the system FeCl₂-FeS_n-H₂S-HCl was described by Lukes, Prutton, and Turnbull,¹⁶ while studies of the rates of formation of ferrous chloride and iron sulphide in the corresponding hydride atmospheres were described by Prutton, Turnbull, and Dlouhy.¹⁷ A description of the shock test has been given by Prutton and Willey.¹⁸ Fig. 1 shows the Chevrolet car as it is assembled for the shock test.

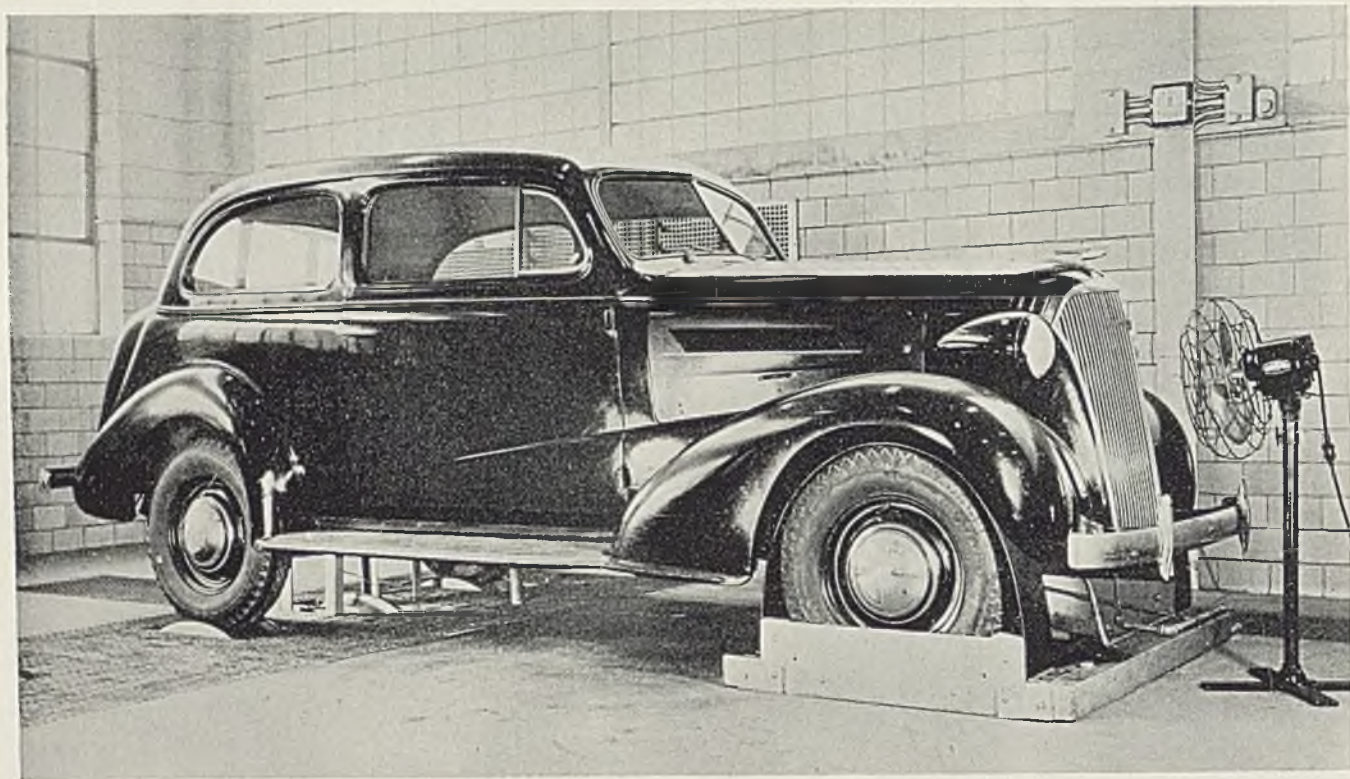


FIG. 1.

CHEVROLET CAR ASSEMBLED FOR SHOCK TEST

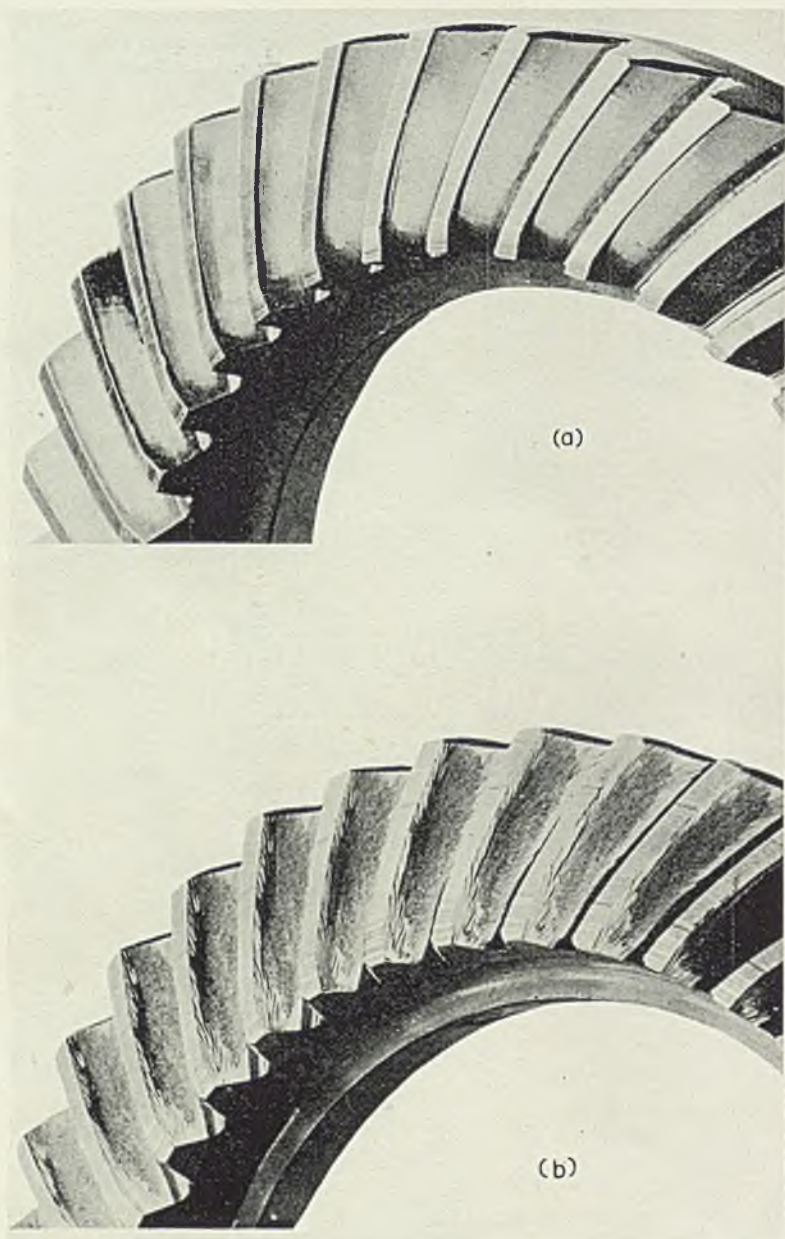


FIG. 2.

(a) SECTION OF GEAR TEETH WHICH PASSED SHOCK TEST. (b) SECTION OF GEAR TEETH WHICH FAILED SHOCK TEST.

Tests on the Stability of Additives in Oil Solution. A number of tests were made in order to measure the thermal decomposition of additive compounds to form HCl and H₂S in oil solution. To this end, 50 cc of an oil solution of the additive were placed in a stoppered 9 in × 1½ in pyrex tube and hydrogen passed through. A fritted glass diffuser was placed on the end of the inlet tube in order to insure that the oil would be saturated with hydrogen at all times. Temperatures were maintained constant to within ± 1° C. during the 15-minute period of the test by means of an electrically-heated oil bath. Exit gases from the chlorine additive solutions were passed through a water absorber in which the HCl formed by decomposition of the additive was collected. H₂S formed from the sulphur additives was collected in an absorption tube containing ammoniated zinc sulphate solution. Contents of the absorption tubes were then analysed for either sulphides or chlorides. Other tests were made in a similar manner, excepting that hydrogen chloride was used in place of hydrogen on the sulphure additive, and hydrogen sulphide on the chlorine additive.

Tests on the Stability of Additives in the Presence of Iron. Another series of stability tests were conducted in order to determine the reactivity of the additive compound towards iron in the temperature range 150 to 250° C. Five gm of electrolytic iron powder, from which traces of oxide were removed by heating for several hours at 800° C. in a hydrogen atmosphere, were used for this test. Reactants, consisting of the iron powder and a 50-cc solution of additive in oil, were placed in a 150-cc pyrex two-neck, round-bottom flask. Stirring was obtained by a motor-driven glass stirrer passing through a mercury seal in one neck.

Analytical Methods. Chlorides were determined by potentiometric titration. Hydrogen sulphide and normal iron sulphide (FeS) were determined by the evolution method described in the A.S.T.M. Designation E-30-39 pp. 23-26. In instances where some sulphide was formed which was insoluble in HCl (possibly FeS_{1.14}) it was necessary to determine total sulphur by the combustion method.¹⁹ This method consists in burning the sample containing sulphides in a quartz tube at about 1100° C. in a stream of oxygen, passing the gases over platinum gauze, and absorbing them in a caustic solution of known strength containing hydrogen peroxide. From the titre of the remaining caustic, the amount of H₂SO₄ formed was readily calculated. When chloride and sulphide were present together, it was necessary to extract the ferrous chloride with water before this procedure.

Melting Points. Melting points of mixtures of anhydrous ferrous chloride and FeS were taken from cooling curves of these mixtures in Vycor tubes. Temperatures were measured by means of a calibrated chromel-alumel thermocouple and recorded by means of a Leeds and Northrup micromax recorder.

Shock Test Results.

Table I summarizes the results of shock tests of gears lubricated with oil solutions of various sulphur and chlorine additives and combinations of them. Results of these tests are recorded simply as "pass" or "fail," although in tests where "fail" is recorded the failure may have occurred in earlier or later stages of the test, and the "score" marks may have differed

in extent. Fig. 2 (a) is an enlarged photograph of gear teeth taken from a set which passed the test, and Fig. 2(b) is a similarly enlarged photograph of gear teeth from a set which definitely failed the test.

TABLE I.

Results of Shock Tests on Oil Solutions of Sulphur and Chlorine Additives.

Sulphur compound.	% Sulphur from additive in oil.	Chlorine compound.	% Chlorine from additive in oil.	Results.
Elemental sulphur	0.50	None	—	Fail
Benzyl disulphide	0.50	None	—	Fail
Benzyl disulphide	1.00	None	—	Fail
Benzyl disulphide	0.50	Chlorinated paraffin wax	3.00	Pass
Benzyl disulphide	0.50	Chlorinated diphenyl ether	3.00	Fail
None	—	Chlorinated paraffin wax	3.00	Fail
None	—	Chlorinated paraffin wax	6.00	Pass
Sulphur	0.50	Chlorinated paraffin wax	3.00	Pass
Phenyl disulphide	0.50	Chlorinated paraffin wax	3.00	Fail

Oil solutions of sulphur additives did not pass the test for any of the concentrations of additive used. Failure was observed even though the additive may have been quite reactive towards iron. A solution of chlorine additive failed the test at the lower concentration, but passed the test at double this concentration. Solutions which contained both active sulphur and chlorine additives at the lower concentration passed the test satisfactorily. This serves to emphasize a co-operation between chlorine and sulphur additives in gear lubrication by which the shock test is passed when sulphur and chlorine compounds are present in the same oil solution, while the test is not passed when either of the additives is present separately at the same concentration. It is to be observed further that definite limitations exist upon the type of chlorine and sulphur additive combination passing the shock test. Thus, although chlorinated paraffin wax in conjunction with benzyl disulphide passes the test, when chlorinated diphenyl ether (in which all chlorine is attached to the benzene ring) is used to supply the same amount of chlorine as the chlorinated paraffin wax the test fails. Also when phenyl disulphide supplies the same amount of sulphur as the benzyl disulphide, its combination with the same amount of chlorinated paraffin wax fails the test.

Examination of Gear Teeth and Axle Drains.

In order to establish definitely that chemical interaction between gear teeth and chlorine-sulphur additive solutions occur in service, gear teeth were analyzed for iron sulphide and ferrous chloride after having been subjected to a shock test in which a commercial chlorine-sulphur extreme-pressure lubricant was used. These results showed that 1.3 milliequivalents of ferrous chloride and 3.1 milliequivalents of iron sulphide per square meter of area remained on the teeth after the shock test.

To further confirm this interaction, a used lubricant from a shock test, in which a commercial chlorine-sulphur lubricant was employed, was

analysed for the iron sulphide and ferrous chloride suspended in it. These analyses, which were run in duplicate, showed 0.61 milliequivalent of ferrous chloride and 0.06 milliequivalent of iron sulphide per 1000 gm of used lubricant. These tests demonstrate that iron sulphide and ferrous chloride are actually formed in service by interaction of the additive with the gear teeth. They further demonstrate that about ten times as much ferrous chloride as iron sulphide is "rubbed off" into the oil during service.

Analyses were also made for suspended iron sulphide and ferrous chloride in the used lubricant from a high torque test in a Dodge truck axle in which a commercial chlorine-sulphur lubricant was used. In the high torque test (C.R.C. Designation L-20-545 Test Procedure for Determining the Load Carrying Wear, Stability, and Corrosion Characteristics of Universal Gear Lubricants in Axles under Conditions of High Torques and Low Speeds), a ring-gear speed of 62 r.p.m., ring-gear torque of 32,311 inch-pounds and a test duration of 30 hours, are used. In 1000 gm. of the used lubricant, 1.9 milliequivalents of ferrous chloride and 0.02 milliequivalents of iron sulphide were found. In this test, where lower temperatures probably prevail at the points of actual contact than in the shock test, it is apparent that an even larger proportion of ferrous chloride to iron sulphide is rubbed off the gear teeth during service.

Decomposition of Sulphur Compounds in Oil Solution and on Iron Powder.

To aid in explaining the mechanism of co-operation between chlorine and sulphur additives in gear lubrication, a thorough understanding of the mechanism of interaction of sulphur and chlorine additives singly with iron was highly desirable. To this end stability studies were made on various additives present alone in oil solutions in the presence and in the absence of iron powder, in the temperature interval 150-250° C.

Reactivity of Sulphur Additives.

Table II shows the extent of decomposition of various sulphur additives in oil (S.A.E. 90) solution where concentrations of sulphur additives were adjusted to 0.5 per cent added sulphur in all cases. Two test conditions at 250° C. were employed. In the first, hydrogen gas was passed through the solution for 15 minutes, and in the second, the effects of 15 minutes exposure to iron powder in a nitrogen atmosphere were examined.

TABLE II.
Reactivity and Decomposition of Sulphur Additives at 250° C.

Sulphur additive.	% of S in additive forming H ₂ S in H ₂ (no iron).	% of S in additive which reacts or decomposes on iron powder.		
		Total.	% which forms H ₂ S.	% which forms FeS.
Benzyl disulphide	3.9	45.5	0.73	44.8
Amyl disulphide	0.79	12.9	0.90	12.0
Amyl monosulphide	0.51	4.5	0.41	4.1
Phenyl disulphide	0.74	4.4	4.0	0.37
Phenyl monosulphide	0.39	3.6	3.2	0.41

From Table II it is apparent that in most cases decomposition of the additive in a stream of hydrogen in the absence of metal is either quite small or entirely insignificant at 250° C. Free sulphur itself will interact with heated oil readily at this temperature to form H_2S . It is apparent that in all cases iron powder greatly increases the elimination of sulphur from sulphur additives. For all compounds excepting the entirely aromatic sulphides this increase can be accounted for by direct reaction of additive with iron to form iron sulphide. For the entirely aromatic compounds, however, very small amounts of iron sulphide were formed, but the evolution of H_2S was greatly increased. This behaviour was also observed in experiments at 200° C.

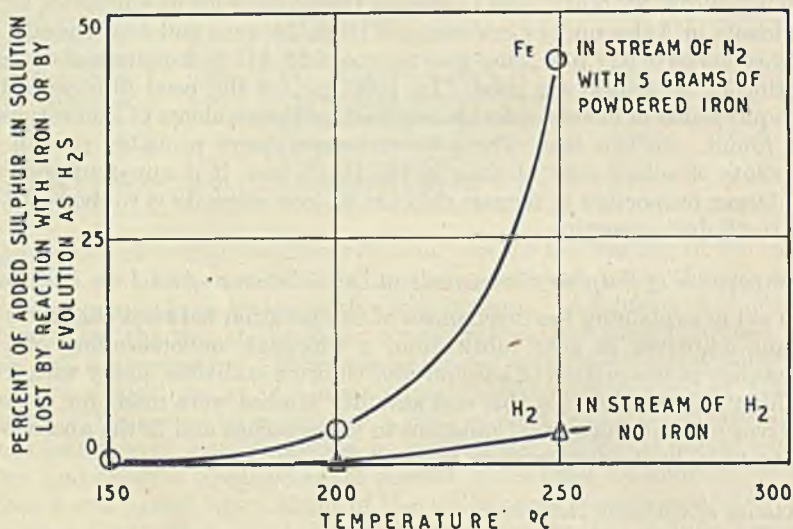


Fig. 3.

REACTIVITY OF DIBENZYL DISULPHIDE. 15 MINUTE TEST, 50 GRAMS OF A SOLUTION OF DIBENZYL DISULPHIDE IN MID-CENTINENT S.E.A. 90 OIL, 0.5 PER CENT ADDED SULPHUR BY WEIGHT IN SOLUTION.

Fig. 3 shows the reaction and extent of decomposition of benzyl disulphide as a function of temperature in an atmosphere of hydrogen, both in the presence and in the absence of powdered iron. These curves exhibit shapes which are typical of those shown by other sulphur additives of low and intermediate activity. It is apparent that up to 200° C. this additive is quite stable in the absence of iron, although substantial amounts of iron sulphide are formed on iron powder at this temperature. As might be anticipated, an exponential relation between the extent of reaction and $1/T$ is approached.

Of considerable importance in considering the mechanism of interaction of sulphur additives with iron is the mechanism of iron sulphide film growth. This was discussed thoroughly in a previous paper,¹⁷ in which were reported data for the reaction rate of hydrogen sulphide with iron in the temperature range 250–350° C. These data indicated that growth of iron sulphide films involved: (1) diffusion of iron ions and electrons outward through the iron

sulphide lattice to the surface of the film; (2) chemical reaction of iron at the outer surface either with the sulphur compound or elementary sulphur formed by the dissociation of the compound. Iron sulphide films offer comparatively little resistance to the passage of iron ions, so that in gear lubrication the problem must be faced of selecting a sulphur additive or a combination of sulphur and chlorine additives, which will not attack iron rapidly at lower temperatures.

Reactivity of Chlorine Additives.

Table III shows the extent of reaction and decomposition of various chlorine additives when hydrogen is passed through the solution both in the presence and in the absence of iron powder at 250° C. for a 15-minute period. In each solution, sufficient additive was added to yield a chlorine concentration of 3 per cent by weight.

TABLE III.
Reactivity and Decomposition of Chlorine Additives at 250° C.

Chlorine additive.	% of Cl in additive forming HCl in H ₂ (no iron).	% of Cl in additive which reacts or decomposes on iron powder.		
		Total.	% which forms HCl.	% which forms iron chloride.
Chlorinated paraffin wax	2.40	10.7	4.3	6.4
Chlorinated diphenyl ether	0.20	0.06	0.04	0.02

In this group of additives it is apparent that the chlorinated diphenyl ether is almost completely inactive towards both hydrogen and iron at 250° C. Appreciable activity in liberating HCl or attacking iron is shown by the chlorinated paraffin wax, however. Iron powder (or ferrous chloride) markedly accelerates the decomposition of this more active additive. Thus the total decomposition of chlorinated paraffin wax is more than four times as great on iron powder as in the absence of iron. At this temperature approximately equal amounts of ferrous chloride and HCl are formed in the presence of iron powder. At 200° C., however, the amount of ferrous chloride formed with iron powder present greatly exceeded the amount of HCl with each of the chlorine-containing additives.

Fig. 4 shows a comparison of the extent of decomposition and reaction of chlorinated paraffin wax on iron powder, and decomposition in hydrogen in the absence of iron at various temperatures. These curves are similar in shape to those for sulphur additives in which the total extent of reaction was low or intermediate. There is an important difference in the temperature variation of the decomposition of chlorinated paraffin wax and benzyl disulphide on iron powder, in that the temperature coefficient of the disulphide is 3.3 times as great as that for the chlorine additive in the range 200–250° C.

Mechanism of Growth of Ferrous Chloride Films on Iron.

In a previous paper¹⁷ the mechanism of growth of ferrous chloride films in an atmosphere of hydrogen chloride was discussed. A mechanism for

the growth of such films was postulated as follows: (1) adsorbed HCl on the ferrous chloride diffuses through the gross structural defects of the film (pores, fissures, grain boundaries); and (2) reacts with the iron at the film-metal interface. Since the lattice itself apparently does not permit the passage of any appreciable quantity of reactant, ferrous chloride films will tend to thicken much more slowly than iron sulphide films, even though the chemical activity of the sulphur and chlorine reagent may be similar.

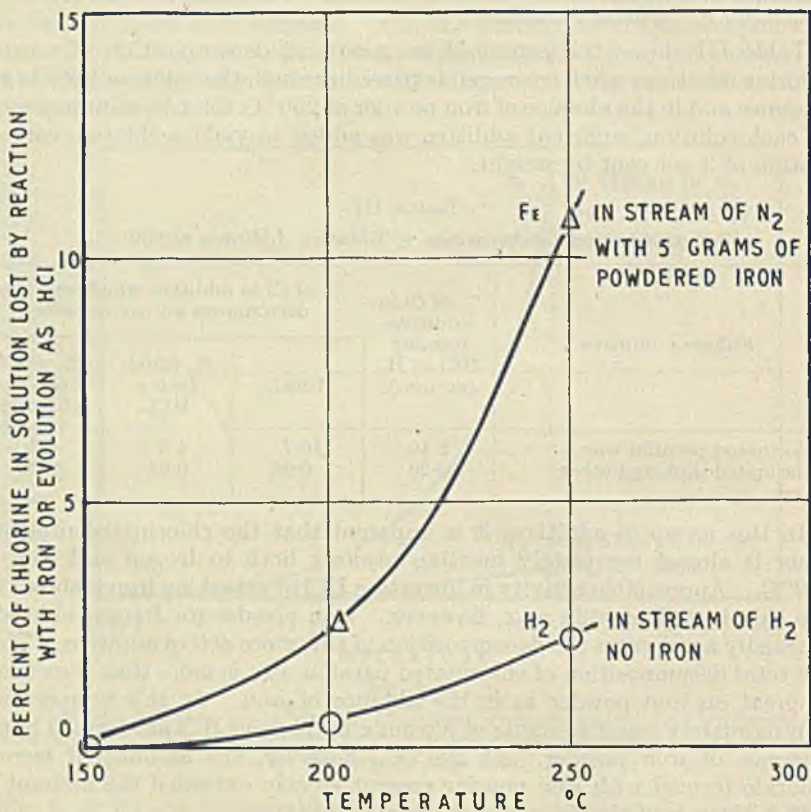


FIG. 4.

REACTIVITY OF CHLORINATED PARAFFIN. 15 MINUTES TEST, 50 GRAMS OF A SOLUTION OF CHLORPARAFFIN IN MID-CONTINENT S.A.E. 90 OIL, 90 PER CENT CL BY WEIGHT IN SOLUTION.

Thus ferrous chloride films, where formed, offer a protection against further attack by the chlorine additive.

Decomposition of Chlorine and Sulphur Additive Combination by Hydrogen.

To study the mechanism of co-operation of sulphur and chlorine additives, an investigation was made of the possibility that one might catalyze the decomposition of the other in oil solution. For this purpose hydrogen under 1 to 2 atmospheres pressure was passed through oil solutions containing a chlorine additive and a sulphur additive singly and then together.

These tests showed that the amounts of HCl and H₂S evolved from the solution containing both sulphur and chlorine additives were not markedly different from the amounts which would have been formed by the action of hydrogen on the solution of the corresponding single additive.

Effect of H₂S upon Decomposition of Chlorine-Sulphur Additive Combination by Hydrogen.

To test more thoroughly the possibility that H₂S produced in the decomposition of sulphur additive might catalyze the decomposition of chlorine additive, the amount of HCl formed by a 1 : 1 mixture of hydrogen and hydrogen sulphide passing through the oil containing both additives at 250° C. was measured and compared with that evolved by a 1 : 1 mixture of hydrogen and nitrogen under the same conditions. These results indicated that H₂S had no positive catalytic effect upon the decomposition of the chlorine additive.

Effect of HCl upon Decomposition of Chlorine-Sulphur Additive Combination by Hydrogen.

Also tested in a similar way was the possibility that HCl produced in the decomposition of the chlorine additive might catalyze the decomposition of the sulphur additive. It was found that about eight times as much H₂S was formed by a 1 : 1 mixture of hydrogen and hydrogen chloride passing through the benzyl disulphide solution as was formed by a 1 : 1 mixture of hydrogen and nitrogen passing through the same solution. Thus HCl apparently has a marked positive catalytic effect upon the decomposition of the sulphur additive. However, decomposition of the sulphur additive in the presence of HCl is only about $\frac{1}{10}$ as large as the reaction and decomposition obtained on iron powder under similar conditions. Therefore, the amount of reaction of sulphur additive on iron powder is probably of much greater significance than H₂S evolution catalysed by HCl.

Decomposition of Chlorine-Sulphur Additive Combinations on Iron Powder.

Table IV summarizes the results of the studies of the reaction of various combinations of chlorine and sulphur additives in white oil solution on iron powder at 250° C. When sulphur additives were used alone, the sulphur contents of the powder as determined by the evolution and combustion methods agreed within experimental error. In the presence of chlorine additive, however, it was observed that with very reactive sulphur additives after analysis of the iron powder by the evolution method, a black residue remained which was insoluble in HCl. It was suspected that this material was some higher sulphide of iron, such as FeS_{1.14}. Analyses of these samples for total sulphur by the combustion method confirmed the presence of much more sulphur than found by the evolution method which presumably measures only the amount of FeS.

Results shown on Table IV point to certain conclusions which are highly significant in indicating the mechanism of co-operation of sulphur and chlorine compounds. It is observed that when an active sulphur additive (such as benzyl disulphide or sulphur itself), which in the absence of chlorine additive would form relatively large amounts of iron sulphide, acts in

TABLE IV.

Comparison of the Reactivity of Chlorine and Sulphur Additive Solutions (0.50 per cent Sulphur and 3.00 per cent Chlorine) in White Oil on Iron Powder (5 gms.) at 250° C. Singly and in the Presence of Each Other.

Chlorine additive.	Sulphur additive.	Milliequivalents of ferrous chloride formed.		Milliequivalents of HCl formed.		Milliequivalents of iron sulphide formed.		Milliequivalents of H ₂ O formed.		
		With S additive.	Without S additive.	With S additive.	Without S additive.	With Cl additive.		Without Cl additive.	With Cl additive.	Without Cl additive.
						Combustion method.	Evolution method.			
Chlorinated paraffin wax .	Benzyl disulphide	2.55	1.30	2.97	2.41	0.40	0.01	11.6	0.127	0.065
Chlorinated paraffin wax .	Sulphur	3.16	1.30	2.83	2.41	3.00	0.71	16.2	3.8	0.124
Chlorinated paraffin wax .	Phenyl disulphide	1.35	1.30	3.00	2.41	—	0.00	0.067	0.137	0.175
Chlorinated paraffin wax .	Phenyl sulphide	1.44	1.30	2.64	2.41	—	0.015	0.098	0.011	0.052
Chlorinated diphenyl ether .	Benzyl disulphide	0.06	0.07	0.99	1.19	—	9.6	11.6	0.067	0.065
Benzo trichloride *	Benzyl disulphide	5.87	1.23	4.79	1.49	—	0.00	0.82	0.03	0.00
Chlorinated paraffin wax *	Benzyl disulphide	—	—	1.32	1.17	—	—	—	—	—

*. Tests were conducted at 200° C.

conjunction with chlorinated paraffin wax, the quantity of ferrous chloride formed is substantially larger, by a factor of about 2, than that formed by chlorinated paraffin wax acting by itself. It will be noted that for the active sulphur additive, H_2S evolution is nearly unaffected by the presence of the chlorine additive. Any change in H_2S evolution resulting from the presence of the chlorine additive is very much less than the increase in ferrous chloride formation. Elemental sulphur, however, is an exception since in that case the increase in H_2S evolution with the chlorine additive present is more than equivalent to the increase in the amount of ferrous chloride formed.

Another very noteworthy feature of these results is that the active chlorine addition reduces the amount of sulphide in the film to a very small proportion ($\frac{1}{10}$ in the case of benzyl disulphide) of that formed by the sulphur additive acting alone. Thus, using benzyl disulphide and chlorinated paraffin wax together, about four-fifths of the film is ferrous chloride. Even with elemental sulphur, which is very reactive toward iron, the film is more than one-half ferrous chloride. These results are in agreement with the observations of Prutton, Turnbull, and Dlouhy,¹⁷ who reported that the presence of ferrous chloride in a film on iron "inhabited" the formation of ferrous sulphide. This decrease in iron sulphide content is not compensated for by a corresponding increase in the amount of ferrous chloride formed. For example, in the case of benzyl disulphide the amount of iron sulphide formed was only about one twenty-fifth as much as when the chlorinated paraffin wax was present. The solution containing both benzyl disulphide and chlorinated paraffin wax formed about twice as much ferrous chloride as did the solution with chlorinated paraffin wax alone.

Evolution of HCl by chlorinated paraffin wax at 250° C. in this test was not significantly affected by the sulphur additive. In the absence of any sulphur additive, 2.4 milliequivalents of HCl were evolved from chlorinated paraffin wax solution, and when various sulphur additives were added to this solution the average amount evolved was 2.6 milliequivalents. The deviation of HCl evolution from 2.4 was in no case greater than 25 per cent.

In the presence of iron, benzotrichloride, one of the compounds found by Davey to be most effective in the lubricant test on the "Shell" four-ball machine, evolved much more HCl than does chlorinated paraffin wax under identical conditions. Table IV shows that at 200° C., a solution of benzotrichloride (containing 3.0 per cent Cl) evolved 1.49 milliequivalents of HCl, while two samples of chlorinated paraffin wax (Anglamol 40) evolved 1.17, respectively. In the presence of benzyl disulphide, benzotrichloride solution evolved 4.79 milliequivalents of HCl, while chlorinated paraffin wax with benzyl disulphide liberated only 1.32 milliequivalent of HCl.

Results obtained with elemental sulphur and with the more active sulphides indicated that the catalytic effect of sulphur additives in increasing the rate of formation of ferrous chloride was roughly in proportion to the activity of the sulphur additive in forming iron sulphide. From this it was supposed that less active organic sulphides would not be very effective in increasing the amount of ferrous chloride formed in this test, and Table V shows that this is the case for aromatic mono- and disulphides. These sulphides formed less than 0.1 milliequivalent of iron sulphide in the absence of chlorine additive, and with chlorine additive the increase in the

TABLE V.

Variation of Reactivity of Benzyl Disulphide in White Oil Solution of Chlorinated Paraffin Wax (3.00 per cent Chlorine) on Iron Powder at 250° C. with Concentration of Sulphur Additive.

% Sulphur.	Milliequivalents of ferrous chloride formed.		Milliequivalents of HCl formed.		Milliequivalents of iron sulphide formed.		Milliequivalents of H ₂ S formed.	
	With S additive.	Without S additive.	With S additive.	Without S additive.	With Cl additive.	Without Cl additive.	With Cl additive.	Without Cl additive.
0.05	1.26	1.30	2.53	2.41	0.00	1.41	0.028	0.003
0.15	1.65	1.30	2.20	2.41	0.00	3.96	0.030	0.029
0.50	2.55	1.30	2.97	2.41	0.01	11.62	0.127	0.065
1.50	3.56	1.30	1.83	2.41	0.19	29.2	0.83	0.160

amount of ferrous chloride formed was less than 0.2 of a milliequivalent in both cases.

In line with this view of the rôle of active sulphur additives in catalyzing ferrous chloride formation decreasing the percentage of sulphur additive should decrease the amount of ferrous chloride formed. In order to test this a series of experiments was performed on iron powder at 250° C. in which different percentages of benzyl disulphide were dissolved in white mineral oil containing the standard percentage of chlorinated paraffin wax. Table V summarizes the results of these tests. Iron sulphide contents reported in this table were determined by the evolution method.

Results shown in Table V clearly substantiate the conclusions drawn from those in Table IV and further show that the increase in the amount of ferrous chloride formed in the presence of active sulphur additive increases with the sulphur additive concentration.

Relatively inactive chlorine compounds are little affected by active sulphur additives at 250° C., and in turn exert very little effect on the interaction of sulphur additives with iron at this temperature. This is shown in Table IV by the results of stability tests on chlorinated diphenyl ether. A negligible amount of ferrous chloride was formed either in the presence or in the absence of sulphur additive, and in this instance the amount of iron sulphide formed by the joint action of the two compounds was but little reduced, while the H₂S evolved was unchanged.

From the results of Table V it appeared that a plausible mode of catalysis of ferrous chloride formation by the sulphur additive consisted in the formation of iron sulphide which might then react rapidly with the chlorine additive. If this supposition were true, then the chlorine additive should react with iron sulphide coated iron powder more rapidly than with the uncoated powder. In order to test this supposition, solutions of active chlorine additives were permitted to react with a charge of iron powder which had been coated with sulphide by the action of a 3 per cent benzyl disulphide solution for a fifteen-minute period at 250° C. to produce a heavy film of iron sulphide on the iron. Similar treatment at 200° C. was also employed to produce a relatively thin sulphide coating. After coating, the powder was washed free of the disulphide solution with benzene and ether, and then dried.

TABLE VI.

Products of Reaction between Chlorine Additive Solutions (3.00 per cent. Chlorine) in White Oil and 5 gm. of Iron Powder Coated with Iron Sulphide after a 15-minute Period.

Chlorine additive used.	Meqs. iron sulphide initially present on sulphide coated iron powder.	Meqs. sulphur accounted for after reaction.				Meqs. ferrous chloride formed on iron powder.	Meqs. ferrous chloride on sulphide coated iron powder.	Reaction temperature, ° C.
		FeS by evolution method.	FeS _n by combustion method.	S evolved as H ₂ S.	Total sulphur.			
Chlorinated paraffin wax—Lot "A" .	11.6	—	—	0.12	—	1.30	3.52	250
Chlorinated paraffin wax—Lot "B" .	9.65	8.65	9.1	0.07	9.17	—	2.15	250
Chlorinated paraffin wax—Lot "B" .	1.2	0.32	—	0.02	—	—	2.3	250
Benzo trichloride	12.8	8.8	11.7	0.07	11.8	1.38	4.1	200
Benzo trichloride	11.6	8.7	10.7	0.07	10.8	1.38	3.6	200
Benzo trichloride	1.2	0.10	1.1	0.05	1.1	1.38	4.4	200

Table VI summarizes the results of these experiments which clearly demonstrates that iron sulphide does catalyze the formation of ferrous chloride. In line 1 of this table, it is shown that while 3.5 milliequivalents of ferrous chloride are formed on the sulphide-coated powder by chlorinated paraffin wax solution, only 1.3 milliequivalents are formed on the uncoated powder. Reaction of sulphur and chlorinated paraffin wax solution on uncoated iron powder gave an almost identical amount of ferrous chloride, namely 3.16, as compared with 3.5 milliequivalents of ferrous chloride. Further, benzotrichloride forms about 4 milliequivalents of ferrous chloride on the coated powder, as compared with 1.4 on the uncoated powder. From these results, it appears highly probable that the catalytic effect of active sulphur additive upon ferrous chloride formation is due to the iron sulphide which it forms.

Iron sulphide may promote the formation of ferrous chloride in one of the following ways :

(1) It may "activate" the chlorine additive and cause it to react more rapidly with iron without itself being transformed. If this were true the amount of iron sulphide (FeS), as measured by the evolution method, should be the same before and after reaction with the chlorine additive;

(2) According to reaction (f) of the introduction. In this case an amount of H_2S should be evolved equivalent to the amount of ferrous chloride formed;

(3) According to reaction (g) of the introduction. If the displaced sulphur of this reaction goes into the oil, a decrease in the amount of iron sulphide present equivalent to the amount of ferrous chloride formed should be observed. If the sulphur remains physically entrained in the film or reacts with FeS to give FeS_n , then again the amount of FeS (as detected by the evolution method) should decrease by a quantity equivalent to the ferrous chloride formed, while the total sulphide as detected by the combustion method should remain the same as before the reaction. On the other hand, if all of the displaced sulphur reacts further with iron to form FeS , the sulphur content as measured by the evolution method should be the same before and after the reaction.

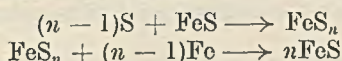
In order to test these hypotheses it was of interest to obtain a sulphur balance after the reaction of the sulphide-coated powder with chlorine additives. Results of this balance for two active chlorine additives are shown in lines 2, 4, 5, and 6 of Table VI. From these results, it is immediately clear that the proportion of H_2S evolved to ferrous chloride formed is in all cases very small (ca. $\frac{1}{30}$). This seems to rule out the possibility that HCl is intermediate in the reaction between iron sulphide and the chlorine additives. In further confirmation of this, it was found that when chlorinated paraffin wax solution reacted with Baker's U.S.P. powdered iron sulphide at 250°C . the amount of H_2S evolved was only 0.5 per cent equivalent to the amount of ferrous chloride formed.

Examination of the results of the reaction of benzotrichloride with the iron powder coated heavily with sulphide (lines 4 and 5—Table VI) shows that the decrease in the amount of FeS (as measured by the evolution method)

is very nearly equivalent to the ferrous chloride formed [on the average $\Delta \text{FeS} = -3.5$ and $\Delta \text{FeCl}_2 = 3.9$]. These data demonstrate that with this additive FeS is actually transformed in the reaction, and that most of the "displaced" sulphur did not have the opportunity of reacting further with iron to regenerate iron sulphide. Determination of total sulphur after reaction showed that most of the displaced sulphur (about 75 per cent.) had remained in the film and apparently combined with FeS to form FeS_n . A black residue insoluble in HCl, presumed to be FeS_n , remained after analysis by the evolution method.

Results of the reaction of chlorinated paraffin wax (line 2, Table VI) with iron powder heavily coated with sulphide again show that about 75 per cent of the displaced sulphur remains in the film. In this case, however, the decrease in the amount of FeS was only 50 per cent equivalent to the amount of ferrous chloride formed, showing that half of the displaced sulphur had the opportunity to react with iron to regenerate FeS. Analysis of the chlorinated paraffin wax solution plus the washings of the residue gave 0.7 milliequivalents of sulphur. This shows that the remainder of the displaced sulphur either remained entrained in the film as elemental sulphur, and was extracted by the benzene wash, or went into the oil phase by dissolution or chemical reaction. Thus a total of 9.87 milliequivalents of sulphur was found after the reaction as compared with 9.65 before. This small discrepancy (2.3 per cent) is well within the analytical uncertainties.

Since most of the sulphur displaced by the reaction of chlorine additive and iron sulphide seems to remain in the film, it appears that a rather small amount of iron sulphide or a thin film of this material may be as effective as a catalyst as a comparatively large amount or a heavy coating. For, if sulphur remains in the film, FeS may continually be regenerated by reactions of the following character :



Some of the experimental data given in Table V definitely point to this conclusion. For example, in the reaction of benzotrichloride and benzyl disulphide with iron powder at 200°C ., about 4 milliequivalents of ferrous chloride were formed in excess of that which would have been formed by the benzotrichloride alone; yet only one milliequivalent of iron sulphide was formed by the reaction of a solution containing only benzyl disulphide with iron at this temperature.

To further test this possibility, solutions of chlorine additive were permitted to react with iron powder very lightly coated with sulphide. Results of these experiments are given in lines 3 and 6 of Table VI. These data, particularly those for benzotrichloride, demonstrate conclusively that only a very thin film of iron sulphide (containing an amount considerably less than the quantity of ferrous chloride subsequently formed) is necessary for catalysis. For benzotrichloride the ferrous chloride increment alone is three times as great as the iron sulphide initially present, while for the chlorinated paraffin wax the total amount of ferrous chloride formed is double the iron sulphide originally present. It is to be noted that most of the FeS originally present has been transformed in these reactions, and that with benzotrichloride most of it has apparently been changed to FeS_n .

Observations were also made on the rate of reaction of a sulphur additive with iron powder coated with ferrous chloride. To form this coating, iron powder was permitted to react with a 50 per cent solution of chlorinated paraffin wax in white oil at 250° C. for $\frac{1}{2}$ hour. After washing with a benzene-ether mixture and drying, five grams of this product were permitted to react with benzyl disulphide solution at 250° C. in the same manner as iron powder. In this test 1.9 milliequivalents of iron sulphide were formed as compared with 11.6 milliequivalents which would have been formed by the action of the same solution on pure iron powder. This fully confirms the supposition that ferrous chloride films inhibit the attack of active sulphur compound on iron. Less than 0.01 milliequivalents of HCl were evolved in this test, which indicates that H_2S is not intermediate in the reaction of the sulphur additive on iron.

While a complete study was not made on the kinetics of formation of films from oil solutions containing both sulphur and chlorine additives, the investigation of the rate of growth of these films in a 1 : 1 mixture of HCl and H_2S gases, previously reported, offers pertinent information about their growth from additive solution. Results of these studies in the vapour phase indicated that ferrous chloride in the film markedly inhibits the rate of formation of iron sulphide by hydrogen sulphide. Thus the very slow reaction with iron of an active sulphur additive in the additive mixture is probably due to inhibition by ferrous chloride.

Melting Points of $FeS-FeCl_2$ Mixtures. In order to test the possibility that lubrication might be accomplished by a low melting eutectic of iron sulphide and ferrous chloride formed by the active additives, melting points of several mixtures of iron sulphide and anhydrous ferrous chloride were measured (mixtures contained 90, 67, and 50 mole per cent of $FeCl_2$). In all these mixtures solidification was found to be complete at temperatures only 5–10° C. lower than the melting point of pure ferrous chloride.

DISCUSSION.

Mechanism of Reaction of Chlorine Additives with Iron.

In the introduction to this paper two apparently plausible mechanisms for the interaction of chlorine additives with iron were suggested, one of which involved direct reaction of additive with iron, and the other prior dissociation of the additive to give HCl followed by reaction of HCl with iron. Experimental results on the decomposition of chlorinated paraffin wax in solution and on iron powder indicate definitely that prior dissociation of additive in solution to give HCl is not an important contributory mechanism since the amount of HCl formed in this manner is much less than can be accounted for by the decomposition of additive on iron powder (see Table III). Thus the mechanism of reaction must involve either direct reaction of additive with iron or reaction of HCl formed by the ferrous chloride catalyzed dehydrohalogenation of the chlorine additive. Since ferrous chloride is known to be a dehydrohalogenation catalyst, the latter mechanism might be plausible. On the other hand, the chlorinated diphenyl ether (see Table V) which decomposed to give substantial amounts of HCl on iron formed a negligible quantity of ferrous chloride at 250° C. In this experiment, about 1 milliequivalent of HCl was formed and less than

0.1 milliequivalent of ferrous chloride. This result would be unlikely if HCl were a reaction intermediate, and argues strongly in favour of the mechanism involving direct reaction of additive with iron.

Mechanism of Reaction of Sulphur Additives with Iron.

Possible mechanisms for the reaction of sulphur additive with iron are direct reaction of sulphur additive to yield iron sulphide, or the dissociation of sulphur additive to either H_2S or sulphur followed by reaction with the iron. In these tests, since the decomposition of additive on iron powder was much greater than its decomposition into H_2S in oil solution (see Table II), it is probable that the reaction mechanism does not involve prior dissociation in solution to give H_2S .

Further evidence that hydrogen sulphide is not intermediate in this reaction is offered by some of the data in Table II, which shows that the aromatic mono- and disulphides in this test formed about ten times as many equivalents of hydrogen sulphide as of iron sulphide, and iron sulphide formation was relatively very small in both cases. For the other organic sulphides, it is observed that a major proportion of the additive which decomposed formed iron sulphide under these conditions, and that the amount of iron sulphide thus formed was much larger than for the purely aromatic sulphides. It is, therefore, probable that the reaction mechanism involves either direct reaction of iron with the sulphur in the additive and/or dissociation of additive on the iron or iron-sulphide surface to give sulphur which then reacts with iron (e).

Mechanism of Reaction of Sulphur-Chlorine Additives with Iron.

Any proposed mechanism for the interaction of active-chlorine-active-sulphur additive solutions under the conditions studied must satisfactorily explain the following experimental evidence :

(1) A small proportion of iron sulphide is found in the film relative to the amount of ferrous chloride and relative to the amount which would have been formed by the action of sulphur additive alone ;

(2) With active sulphur additives an amount of ferrous chloride is formed by the joint action of the additives which may be double or triple that formed by the chlorine additive alone, depending upon the activity of the sulphur additive ;

(3) In general an amount of H_2S is evolved during the joint action of the additives, which is much less than equivalent to the increased ferrous chloride content of the film over that formed by the action of the chlorine additive alone ;

(4) When chlorinated paraffin wax reacts with iron sulphide an amount of H_2S is evolved which is less than $\frac{1}{10}$ equivalent to the amount of ferrous chloride formed ;

(5) Chlorinated paraffin wax reacts about two and one-half times as rapidly with iron powder coated with iron sulphide as with iron powder itself of similar grain size. This reaction apparently proceeds almost as rapidly with a light sulphide coating as with a heavier one ;

(6) In the reaction between chlorine additive solutions and FeS coatings on iron powder, the bulk of the displaced sulphur (about

75 per cent.) remains in the film and reacts to regenerate FeS or give FeS_n ;

(7) Sulphur additives which are by themselves comparatively inactive toward iron do not promote the formation of ferrous chloride to any appreciable extent when used in conjunction with an active chlorine additive. As the concentration of an active sulphur additive is increased its catalytic effect in the formation of ferrous chloride is enhanced.

In the introduction, a number of possible modes of co-operation of sulphur and chlorine additives in oil solution were suggested. Some of these can now be eliminated as inconsistent with the experimental evidence just presented. A number of the discussed modes of co-operation involved catalysis of the formation of iron sulphide or sulphur additive decomposition products in a variety of ways. It appears that these may now be eliminated from consideration in view of (1) above, which states that the formation of iron sulphide is inhibited rather than catalyzed due to the presence of a ferrous chloride film.

Remaining then to be considered are the various ways in which the sulphur additive may catalyze the decomposition of the chlorine additive or the formation of ferrous chloride. It has been suggested that the sulphur additive in solution might catalyze the decomposition of the chlorine additive in solution into products which react more rapidly with iron. There is no experimental evidence to indicate that this is the case. When hydrogen was passed through a solution containing both chlorine and sulphur additives, the amount of HCl evolved was not markedly different from that evolved from a solution of the chlorine additive alone. Further, this mechanism, although possibly explaining (1), (2), and (3) in the evidence listed above, offers no explanation of (4), (5), (6), and (7). This mechanism does not involve the iron surface, and most of the points listed, particularly (7), suggest that the surface is involved in the catalytic action.

Mechanism (f) of the introduction, which involves reaction of HCl with FeS_n , seems definitely eliminated by points (3) and (4) above, as explained in the section on results. Of the possible mechanisms suggested, the only one which seems capable of accounting for all of the experimental evidence is summarized by equations (c) or (e) followed by (g) and (g₄). According to this mechanism sulphur additive reacts rapidly with iron powder either directly or by dissociation on the surface to give sulphur, which then reacts to form FeS or FeS_n . Then the iron sulphides react directly by equation (g) with the chlorine additive to give ferrous chloride and sulphur. Most of the sulphur displaced in this reaction remains in the film and forms FeS_n , or regenerates FeS by reacting further with iron according to (g₄). This mechanism presupposes that at higher temperatures: first, the active sulphur additive reacts with iron much faster than the active chlorine additive; second, active chlorine additive reacts with iron sulphide more rapidly than with iron; and third, ferrous chloride is the main constituent of the resultant film.

Point (1) of the experimental evidence is explained in any case by the inhibition of iron sulphide formation by ferrous chloride, as previously noted. Point (2) is explicable on the basis of the presupposition that

chlorine additive reacts more rapidly with iron sulphide than with iron. Agreement between the proposed mechanism and the rest of the experimental points is self-evident. Thus in the light of the experimental evidence the proposed mechanism of co-operation appears entirely reasonable, while the other mechanisms considered are inconsistent with the experimental evidence.

Mechanism of Extreme-Pressure Lubrication by Sulphur and Chlorine Additives.

Although these laboratory stability tests admittedly do not approach conditions existing on the surface of gear teeth during service, they suggest a plausible theory for the co-operation of sulphur-chlorine additives as evidenced by shock tests. Sulphur additives, although they form a much heavier film on an equivalents basis than chlorine additives at elevated temperatures, are not particularly effective as extreme-pressure additives under "shock" conditions (see results of shock tests, Table I). Even elementary sulphur, which is quite reactive at low temperatures, fails the shock test when used alone. This lack of effectiveness of sulphur additives under shock conditions might be attributed to :

(1) excessive wear due to the chemical attack of the gear teeth at points other than actual contact points under high pressure by the sulphur additive ; or

(2) the film formed by sulphur additives (principally FeS) may not melt readily (melting point of FeS = 1193° C.) and may possess high shear strength under shock conditions.

Oil solutions containing chlorinated paraffin wax in sufficiently high concentration will pass the shock test. In the presence of active sulphur additive, however, the concentration of chlorine additive required is cut in half. Since chlorinated paraffin wax by itself is not highly reactive toward iron at elevated temperatures (as compared with sulphur additives) but provides satisfactory extreme-pressure lubrication at high concentrations, it appears that a sufficiently thick ferrous chloride film may be formed to serve as a satisfactory lubricant under shock conditions. With chlorine additives then the problem of extreme-pressure lubrication becomes reduced to selecting conditions under which ferrous chloride may be formed with sufficient rapidity under rapidly applied loads to maintain a film at the contact points. This problem may be solved in several ways : (1) by the use of a sufficient amount of a very reactive chlorine additive, such as C_2Cl_6 , etc., a practice which might very well lead, however, to excessive corrosion of the gear teeth at lower temperatures ; (2) by use of high concentrations of mildly active chlorine additive, which might not be desirable because of the expense and marked alteration of the properties of the oil ; or (3) by the addition of a catalyst which promotes the formation of ferrous chloride at the contact points produced by a less active chlorine additive at lower concentrations ; such a catalyst should not become effective excepting at rather high temperatures.

From the results of this investigation it appears probable that sulphur additives accomplish the last of the solutions (3) proposed in the preceding paragraph by catalyzing (or more properly by forming iron sulphide which

catalyzes) at high temperatures the rapid formation of ferrous chloride. This would imply that the co-operation between chlorine and sulphur additives in extreme-pressure lubrication is due to the rapid formation of a ferrous chloride lubricant film. In suggesting this as the most plausible mechanism, however, the possibility must not be overlooked that the superior extreme-pressure properties of the combination may be due to the particular character or composition of the film formed rather than to the rapid formation of ferrous chloride. Thus the film formed at 250° C. by the combination of chlorinated paraffin wax and benzyl disulphide contained, on an equivalents basis, about 15 per cent of FeS_n (HCl insoluble) and 85 per cent ferrous chloride, and it is possible, although not probable, that such a film might function more satisfactorily under extreme-pressure conditions than either ferrous chloride or FeS_n .

Once formed at the points of actual contact, ferrous chloride films may then reduce friction in two ways: (1) under existing conditions at the contact points solid ferrous chloride may readily shear; (2) temperatures at the contact points may become high enough to melt the ferrous chloride or ferrous chloride containing a small percentage of FeS_n . Overcoming frictional force will then involve shearing only a liquid film of ferrous chloride containing some dissolved FeS_n . It is not possible on the basis of present evidence to decide between these two modes of action, and in fact the difference between them is one of degree rather than kind. Very little data are available on the sheer strength of solid inorganic films at high temperatures, but most solids tend to resist plastic deformation to a much lesser extent as the melting point is approached. Both mechanisms would produce a polishing action, or wearing down of pronounced surface irregularities on the gear teeth. Such a polishing action is observed with sulphur-chlorine hypoid lubricants as with other extreme-pressure agents.^{11, 13} These experiments are clearly indicative of the fact that a polishing action has taken place which has worn down the prominent protuberances and assured lower temperatures at contact areas so that less drastic lubrication is required. Actually, the real contact area is probably the same for a given loading regardless of the polishing, but it should be possible to dissipate the heat much more rapidly from flattened areas than from sharply protruding areas, so that contact temperatures should be less for polished surfaces than for roughened surfaces.

In view of the work of Bowden and Ridler⁹ on the temperatures which may be reached at actual contact points, it is entirely reasonable to suppose that a ferrous chloride film would melt under the conditions prevalent when gear teeth come together. Ferrous chloride melts at 690° C., which is of the same order of magnitude as the contact temperature attained by Bowden and Ridler using mineral oil containing Castrol X and with a much lower loading than would be attained on hypoid gears. On this basis, iron sulphide films would be expected to prove less satisfactory in providing extreme-pressure lubrication, since the melting point of ferrous sulphide (1200° C.) is much higher than that of ferrous chloride.

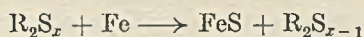
It thus appears that the basic problem in the action of sulphur-chlorine hypoid additives is in forming rapidly a ferrous chloride film at the contact points. Apparently chlorinated paraffin wax by itself (except in very high concentrations) will not form this film rapidly enough to give a continuous

and substantial layer of ferrous chloride before the contact temperatures became high enough to desorb or decompose the reactants. Sulphur additives act to cause the formation of this continuous ferrous chloride film much more rapidly than it can form from the chlorine additive itself by a mechanism outlined above.

In connection with the stability of sulphur additives towards iron it should be noted that when sulphur and chlorine additives are used together, very much less reaction of sulphur additive with iron takes place than would take place in the absence of chlorine additive. Thus, benzyl disulphide was 60 per cent decomposed, mainly by reaction with iron, on iron powder at 250° C. after 15 minutes. In the presence of chlorine additive, however, less than 2 per cent of the additive had reacted with iron in the same period. Thus the normal reactive effect of active sulphur compounds on iron need not be feared in the presence of an active chlorine additive provided that the latter is sufficiently stable in the presence of iron at temperatures around 150° C.

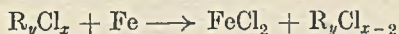
SUMMARY.

1. Reaction of organic sulphides with iron probably takes place by the following mechanism :



It is not possible to ascertain from the present data whether or not there is splitting of the additive on the iron surface to give sulphur prior to reaction.

2. Under mild or slowly applied loads, reaction of organic chlorine compounds with iron probably takes place as follows :



3. In general, iron sulphide films from active sulphur additives form much more rapidly than ferrous chloride films from active chlorine additives at temperatures above 200° C.

4. When both active sulphur and active chlorine compounds are present in oil the following effects are generally observed when interaction with iron takes place :

(a) A rather small proportion of iron sulphide (as FeS_n rather than as HCl soluble FeS) is found in the reaction product relative to the amount of ferrous chloride present ;

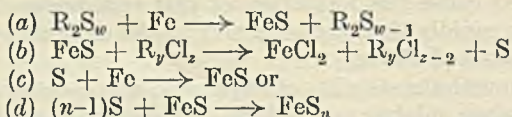
(b) Considerably more ferrous chloride ($1\frac{1}{2}$ to 3 times as much) is formed than would be formed by the action of the chlorine additive by itself ;

(c) For chlorinated paraffin wax HCl evolution is about the same as it is in the absence of the sulphur additive ;

(d) Amounts of H_2S evolved when the additives act together are generally much less on an equivalents basis than the increased amount of ferrous chloride formed.

5. Active chloride additives react more rapidly with iron sulphide or with sulphide-coated iron than with iron itself. Active sulphur additives react much less rapidly with a ferrous chloride coating on iron powder than with iron itself, but this reaction is more rapid than the reaction of chlorine additive with iron.

6. On this basis the following mechanism is proposed for the joint action of active sulphur and active chlorine additives on iron :



These reactions are comparatively rapid, the ferrous chloride is formed more rapidly by this mechanism than by the reaction of the chlorine additive alone with iron, thus providing a lubricant film under shock loading conditions.

7. Ferrous chloride formed by chloride additives represses the excessive action normally associated with active sulphur compounds on iron.

8. It is proposed that extreme-pressure lubrication is accomplished by a combination of sulphur and chlorine additives in the following steps :

(a) As the contact points of the gear teeth heat up, a film consisting principally of ferrous chloride is formed on the points according to the mechanism outlined above ;

(b) As the temperatures become higher, resistance of the ferrous chloride films to shear becomes small, possibly due to fusion (melting point of ferrous chloride = 690° C.) or low shear strength of the solid films at high temperatures.

9. Ferrous chloride formed by chlorine additives represses the excessive action normally associated with active sulphur compounds on iron.

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