Physics. — *Research on thin layers of tin and other metals.* I. *The influence of thin metal layers on the deterioration of technical insulating oils.* By P. J. HARINGHUIZEN and D. A. WAS. (Communicated by Prof. L. S. ORNSTEIN.)

(Communicated at the meeting of October 26, 1935).

Summary.

The influence of metals on the deterioration of insulating oils has been studied. It appeared that on both sludge formation and increase of acidity copper has the largest influence, lead less, and tin the least. In some cases tin may act as an anti-oxidant.

The character of the catalysis has also been a subject of investigation.

A fact known in technics is that the deterioration of insulating oil by oxidation in air is influenced by metals.

The aim of our investigation was to compare the action of tin, copper and lead; we used three transformer-oils of different nature, hereafter indicated by *A*, *B* and *C*.

As sludging and acid formation especially diminish their technical qualities, the influence on these phenomena has been measured.

Nature of the oils:

A	forming	much	sludge,	little	acid	
B	,,	a little	,,	much	,,	
C	,,	a little	,,	little	,,	(etherial acids)

Samples of these oils were deteriorated in glass basins (9 cm), by heating at 90° C. in an electrical furnace; for studying the action of the metals, glass pieces with thin metal layers were dipped into the oils. The metal layers were obtained by high vacuum evaporation [1]); their area was standardised at 5 cm^2.

Sludge formation.

Quantities of 50 c.c. of the oils were heated for 1000 hours and the quantity of sludge formed was measured by filtering through a B_2 crucible; the sludge being washed out with gasoline was dried at 90° C.

Table I gives the quantities of sludge in mgr. per 50 c.c. oil.

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[1]) See publication II of this series.

TABLE I.

Oil	*Sn*	*Pb*	*Cu*	Blank exp.
A	6.0	9.0	19.0	6.9
B	4.0	4.4	5.7	2.0
C	0	2.7	10.2	1.1

These figures show that copper gives the strongest increase in sludge formation, lead less and tin the least. The fact that the oils *A* and *C* in contact with tin formed even less sludge than in the blank experiment. shows that tin may perhaps act as an anti-oxidant; an analogous result has been found by MARDLES [1]) who studied the effect in lubricants.

The colour of the oils.

During the deterioration the oils become darker; now it appeared that after heating for 1000 hours the colours of the (filtered) oils have the same succession as the quantities of sludge.

In the case of oil *A* the authors have determined the colours quantitatively with the aid of the colorimeter constructed by WOUDA [2]).

The values of co-ordinates of the colour points obtained are given in Table II.

TABLE II.

	Original oil	*Sn*	*Pb*	*Cu*	Blank exp.
red	45.1	53.7	55.4	63.1	55.9
green	41.3	41.9	41.0	35.4	42.6
blue	13.4	4.5	3.6	1.4	1.5

From the figure obtained by plotting these values in the known colour triangle the effective wavelength and the saturation of the colour can be determined (see Table III).

TABLE III.

	Orig. oil	*Sn*	*Pb*	*Cu*	Blank exp.
eff. λ	5780	5840	5860	5960	5845
saturation	0.62	0.89	0.92	0.975	0.965

1) E. W. J. MARDLES D. Sc., Techn. Publ. of the Int. Tin Research, Series C N^0. 2.
2) J. WOUDA: Proc. of the Acad. of Amsterdam, Vol. XXXVIII, N^0. 6, 1935.

From a comparison of this table and table I it can be seen that there is a parallelism between sludge formation and eff. λ.

The saturation of the colour forms an exception — "blank exp." being near *Cu* —. The conclusion from this result is that perhaps the increase of eff. λ, which will be caused by polymerisation in the oil, will be followed by sludge formation caused by higher polymerisation of the same complexes. This would explain the parallelism mentioned above.

Acid formation.

Quantities of 100 c.c. oil were heated and after every two hundred hours the acid value was measured according to the method given by the V. D. E.

It appeared that the oil *A* forms very little acid, and oil *C* only etherial acids; in both cases the increase of the acid value was less than the experimental error.

As is pointed out in an investigation on the corrosion of the thin layers (see publ. II of this series) the quantity of acid which is necessary for the corrosion of the metal can be neglected.

Fig. 1 shows the increase of the acid value in the case of oil *B* by deterioration under influence of the three metals.

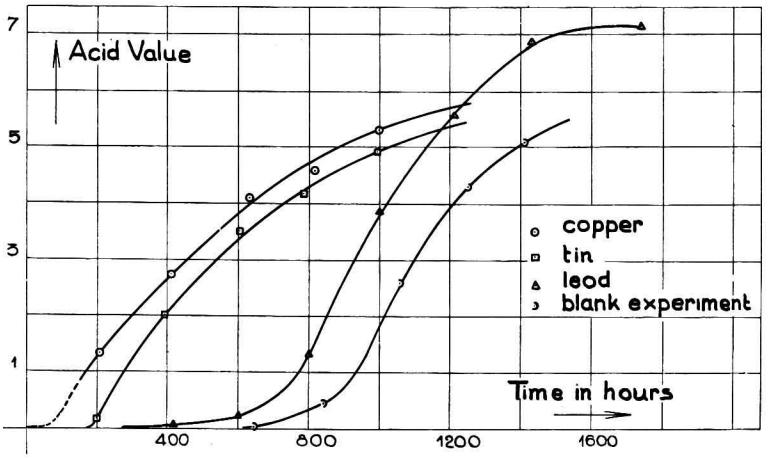

Fig. 1.

It appeared that the increase of acidity due to copper is the greatest; the curve due to tin begins at a later point, after some hundred hours it becomes parallel to that of the one copper. Although the lead curve starts much later, it is much steeper, so that after 1200 hours it even intersects the curves of tin and copper. Parallel to the lead curve runs that of the acid increase in the oil heated without metal.

We have observed a slight increase in acidity in a deteriorated oil, which was left at room temperature without contact with metal; the

relative increase has been found independent of the metal used (see table IV).

TABLE IV.

	Sn	*Cu*	*Pb*
acid value deter. oil	4.94	5.31	1.34
„ „ after 5 weeks room t.	5.28	5.67	1.43
relative increase in %	6.9	6.8	6.7

The character of the catalytic action of metals on oil deterioration.

In order to investigate this character, the following experiments were made:

The acid curve due to copper was measured on three samples of oil *B*. Into each sample an equal copper layer was dipped; the first was taken out after 30 hours, the second after 100 and the third after 450 hours.

In the case of a heterogeneous catalytic action, there must be a great difference between each of the three curves; for after removing the metal surface the catalytic action will be stopped.

In the case of a homogeneous action the removing will not influence the curve, if enough copper is dissolved.

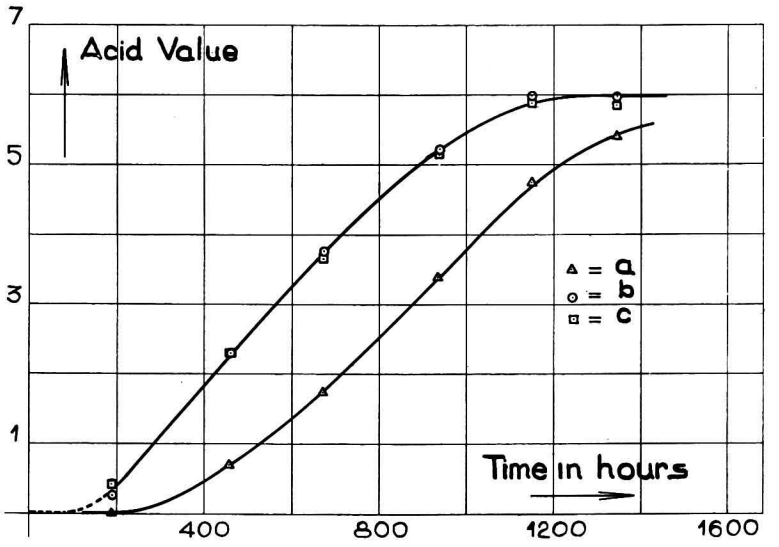

Fig. 2.

The curves *b* and *c* in fig. 2 are the same, so in our case it must be a homogeneous catalysis. The reason that the curve *a* lies lower than *b* and *c*, must be that after 30 hours there is not enough copper dissolved to

reach that range, in which the catalytic action is independent of the quantity of catalysing metal.

In the corrosion investigation (see publ. II) the authors have found subsequently that after about 100 hours copper is no more attacked due to the formation of a protecting film. By this fact it is not excluded that under certain circumstances there can be a heterogeneous catalysis also, viz. if the protecting film is not yet built up or is disturbed by external causes. This will be a subject of further investigation.

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Mathematics. — *Zur Konformgeometrie.* III. *Anwendung auf die Kurventheorie.* Von V. HLAVATÝ. (Communicated by Prof. J. A. SCHOUTEN).

(Communicated at the meeting of September 28, 1935).

In dieser Arbeit werden wir die Konforminvarianten einer Kurve $C(t)$ untersuchen. Dabei benützen wir die Ergebnisse der beiden vorangehenden Arbeiten[1]).

1. Es sei eine Kurve $C(t)$ durch ihre Gleichungen $x^\nu = x^\nu(t)$ in einer K_n gegeben[2]). Diese K_n kann zu einer $\overset{\circ}{W}_n$ gemacht werden, in der die Tensordichte $g_{\lambda\mu}$ kovariant konstant ist

$$\nabla_\omega g_{\lambda\mu} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1,1)$$

(Vergl. K I). Ausgehend von dem Tangentialvektor dx^ν kann man längs C die eichinvariante Einheitsvektordichte (vom Gewicht $1/n$)

$$\underset{1}{i}{}^\nu = i^\nu = \frac{dx^\nu}{\sqrt{|\, g_{\lambda\mu}\, dx^\lambda\, dx^\mu \,|}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1,2)$$

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[1]) V. HLAVATÝ, „Zur Konformgeometrie" I (Proc. Vol. **38**, p. 281), weitert zitiert als K I und V. HLAVATÝ, „Zur Konformgeometrie" II (Proc. Vol. **38**, p. 738) weiter zitiert als K II.

[2]) Nach K I sind die aus $g_{\lambda\mu}$ entspringenden quadratischen Formen d e f i n i t.