

# INVESTIGATION OF THE EFFICIENCY OF INDUSTRIAL DEGREASING METHODS BY RADIOISOTOPE TRACING TECHNIQUE. I

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The good adhesion of coating to metal surfaces is to a great extent inhibited by slight amounts of grease remaining from the preceding processes.

The removal of this impurity consisting of several kinds of grease is carried out by different "degreasing methods". The efficiency of these methods — in case of different types of greases — is an important and, in some respects, unsolved problem.

In this field the success of the investigation is determined by the sensitivities of the chosen methods. In practice none of these differences are to be found among the widespread ways of degreasing (by solvent, alkali or electrolysis) that could be measured by weight. Yet it is obvious that the three methods are not equivalent. This appears from the experience that only the third way results in a perfectly suitable surface for plating; using the other two ways the adhesion of the coating is not found to be satisfactory.

The differences among the efficacies of the three methods can be qualitatively detected by the so-called "water-spreading test" but this can be used only in conjunction with hydrophobic impurities. In case of hydrophil impurities this test can give misleading results (to set an example the wetting additives which are components of the ever more spreading emulsive degreasing agents can cause the hydrophility of the remaining impurities).

According to our investigations a suitable testing of the efficiency of degreasing can be performed by a method based on radioactive indication whose sensitivity surpasses that of the classical test methods by more orders of magnitude.

In order to demonstrate this consider how great initial activity is needed if we want to detect a monomolecular layer on a surface of  $5.14 \text{ cm}^2$ , the lower limit of detection be 100 cpm and the efficiency of counting is 10%. Taking the surface area demand of one molecule  $30 \text{ \AA} = 3 \cdot 10^{-15} \text{ cm}^2$ , the monomolecular layer means

$$\frac{3.14}{3 \cdot 10^{-15}} = 1.05 \cdot 10^{15} \text{ pieces} = 1.75 \cdot 10^{-5} \text{ mole}$$

In case of 1000 dpm, which is considered as minimum, the necessary initial activity is

$$\frac{1000}{1.75 \cdot 10^{-9}} = 5.7 \cdot 10^4 \text{ dpm/mole}$$

this means 275 mC/mole activity. Reckoning e. g. for stearic acid (mole weight 284) approximately 2 mC/g activity is needed. Regarding that  $1.75 \cdot 10$  mole of this substance means round  $5 \cdot 10^{-7}$  g it can be seen what sensitivity is to be expected in the case of a specific activity readily available.

### Grouping of grease impurities

In practice the well-adhering organic impurities occurring on metal surfaces are called greasing impurities. They can be divided into groups according to different principles. In this case the chemical compositions and physical properties of the compounds to be labelled were the bases of their division (Table I).

From the point of view of their chemical compositions the grease impurities to be removed can be divided into four main groups, i. e. glycerides, organic (fatty) acids, paraffin hydrocarbons and products of different chemical compositions. It appears from Table I that in general the grease impurities are not chemically uniform substances in many cases they even belong to different types of compounds (e. g. in abrasive masses glyceride, fatty acid and different sorts of hydrocarbons can occur).

### Radioactive tracing of grease impurities

When choosing the tracer substance the following points of view must be taken into consideration.

*a)* In a given degreasing process there should not be essential differences between the chemical and physical behaviour of the tracer and that of the grease to be traced.

*b)* It must contain a radioactive element, suitable for measuring.

On the basis of these aspects the following possibilities can be taken into account:

1. Tracing with a grease which contains C-14 radioactive isotope.
2. Production and application of a tracer compound or group with I-131 from a grease containing unsaturated bonds.
3. Tracing by mixing in a radioactive metal isotope containing compound soluble in greases (triphenyl antimony, zinc-stearate, zinc-naphtenate).

Table I

Type and Name of Grease Impurities	Chemical Structure	Melting Point	Polarity	Origin of the Impurity
<i>Glycerides</i>				
Rapessed oil (vegetable oil)	erucic acid glyceride oleic acid glyceride linolic acid glyceride	under 20°	partly hetero-, partly homopolar homopolar	at cold forming
Tallow (animal fat)	stearic acid glyceride palmitin acid glyceride oleic acid glyceride	above 20°		at cold forming of aluminium
<i>Organic acid (fatty acids) and their salts</i>				
Stearic acid	stearic acid	above 20°	heteropolar	at pulling wires
Al-stearat	al-stearate	above 20°	heteropolar	temporary defence from perspiring
Lactic acid, butyric acid	lactic acid, butyric acid	under 20°	heteropolar	
<i>Paraffin hydrocarbons</i>				
Paraffin	hydrocarbons with great atomic number (mineral oil products)	above 20°	homopolar	temporary defence
Vaseline	mineral oil products	above 20°	homopolar	temporary defence
Boring oil	hydrocarbons fatty acid (15%)	under 20°	partly homo-, partly heteropolar	at cutting
Cooling-cutting oil	hydrocarbons rapeseed oil (10%)	under 20°	partly heteropolar	at mechanical working
Spindle oil	hydrocarbons	under 20°	homopolar	impurity from greasing the machine
<i>Artificial products of different composition</i>				
Abrasive masses (white, brown, red, etc.)	stearic acid oleic acid tallow wool fat mountain wax carbon wax paraffin machine oil	above 20° above 20° above 20° above 20° above 20° above 20° above 20° above 20°	partly homo-, partly heteropolar	at polishing
<i>Protecting grease against corrosion</i>				
Corrositol	mineral lubricating oil hoof oil calcium stearate	different types are used		
Corrolard	mineral oil products (softening at 60°) machine oil lead stearate	ALT-7. (mp. under 20°) Z-18. (softening 60°) KK-18. (softening 80- 90°)		

4. Neutron-activation of abrasive masses and oil additives having a zinc-content.

5. By means of indirect tracing: detecting the thin grease layer remained after degreasing on the surface by Ag-110 cementing.

6. The application of scintilling oils, that is, using a scintillation measuring instrument after a given illumination [1].

### Tracing with grease of C-14 content [2, 3, 4]

The simplest way of radioactive tracing of greases as organic compounds is to build in C-14 radioactive isotope. Under this circumstance in the given molecule one  $^{12}\text{C}$  atom is replaced by a radioactive C-14 isotope. as in this case no considerable isotope-effect is to be reckoned with, so the tracing of organic compounds can be realized without changing their physical and chemical properties.

The advantage of the long half-life of C-14 in measuring technique is, that it can be regarded as constant even during a longer experimental time (the activity decreases by 1% during 38.6 years). C-14 radiates beta rays of low energy ( $E_{\text{max}} = 0.155 \text{ MeV}$ ), this makes the measuring difficult because there is great self-absorption to be counted with.

In our experiments we used C-14 containing stearic acid whose specific activity was  $0.57 \text{ mC/mmole} = 2 \text{ mC/g}$ . Its radiation could be measured with the greatest sensitivity by a so-called windowless gas-current GM counter (the sensitivity of the current tube proved to be about 10 times greater than that of the beta scintillator).

In the flow counter—eliminating the absorption of the ray through the window of the GM tube — the sample is so deposited, that the beta counting could be carried out by nearly  $2\pi$  geometry. During detection the counter was continuously flushed with "F" argon. Before introducing, the flushing gas had been bubbled through n-amyl alcohol at room temperature. The operating voltage had to be chosen as 1600 V.

One of the consequences of the low energy beta radiation of C-14 is, that the radiation undergoes a significant absorption in the stearic acid layer itself (self-absorption). The half thickness of the C-14 radiation is  $2.6 \text{ mg/cm}^2$  thus in a layer of  $80 \mu\text{g/cm}^2$  the diminution of the intensity is 1%.

From this it follows that stearic acid traced with C-14 is suitable mainly for the studying of these layers of grease. In other cases the self-absorption as a possible cause of correction must always be taken into account.

The maximum and minimum thicknesses of layers applied in the course of our experiments as well as the measured count numbers belonging to them, the errors caused by self-absorption and the statistical errors of the measurements are presented in Table II.

Table II

Thickness of stearic acid layer	Counting number cpm	Relative decreasing % by self-absorption	Standard deviation
$2.64 \cdot 10^{-5}$	39.118	10	0.50
$2.64 \cdot 10^{-7}$	1.090	1	3.16

The C-14 radioactive isotope containing stearic acid of 0.57 mC/mole activity could be measured in a flow GM counter with an error of 3.2% in case of a thickness of  $5.5 \cdot 10^8$  g/cm<sup>2</sup>. This result shows the reality of the informative counting given in the introduction.

### C-14 isotope containing stearic acid as a tracer

Two possibilities are given for the application of C-14 isotope containing stearic acid:

a) The effectivenesses of the different degreasing agents can be followed by using the traced stearic acid alone. Mainly this method is to be found in literature [2].

b) The traced stearic acid is used only as an indicator mixed into other greases. Regarding the fact that stearic acid is well-soluble in different greases this can easily be carried out. Such mixtures may be used because — according to Table I — in practice different sorts of greases must be removed e. g. abrasive masses contain a significant ratio of stearic acid.

Nevertheless the use of stearic acid in such a way is limited by the decrease of sensitivity caused by mixing, at least at moderate specific activities.

Beside stearic acid the C-14 containing glycerin palmitate or palmitic acid are also easily available.

### Tracing by built-in I-131 radioactive isotope

These experiments were initiated by establishing that there are numerous unsaturated compounds among the industrial grease impurities (e. g. the iodine number of colza oil is 95—105, that of tallow is 35—40).

Tracing compound was produced by building-in radioactive iodine (I-131 can be easily obtained). Iodine is connected with the carbon chain of the molecule so the compound to be traced retains all its chemical features but unsaturation (glycerides behave like glycerides and fatty acids like fatty acids also after iodizing).

The half-life of I-131 is 8.1 days. Considering that one degreasing experiment takes three hours as a maximum the greatest possible error from the decreasing of activity is 1.5% during this length of time.

Contrary to C-14 the decay of I-131 produces also well detectable gamma ray. The advantage of this measuring technique is, that there is no need to count with self-absorption even in the case of greases having a greater thickness. The gamma radiation of I-131 can be properly measured with a scintillation counter.

For this purpose greases to be traced linseed oil (iodine number 170—200) and sunflower seed oil from glycerides could be taken into account. Among fatty acids oleic acid was chosen.

The necessary activity of I-131 must be at a level to produce at least 100 cpm in case of  $10^{-7}$  g/cm<sup>2</sup> grease. The way of its reckoning: if we want to achieve 100 cpm, then—taking the effectiveness of counting 25%, — the activity of  $10^{-7}$  g grease must be  $100/0.25 = 400$  dpm. Consequently the traced grease is  $400/10^{-7} = 4 \cdot 10^9$  dpm/g that is approximately 2 mC/g specific activity.

### Production of marked compound by iodizing

Solutions A: 0.3 g sodium iodide (NaI) was dissolved in 10 ml distilled water to which carrier free  $\text{Na}^{131}\text{I}$  of about 4 mC activity was added.

Solution B: 0.4 g sodium nitrite ( $\text{NaNO}_2$ ) was dissolved in 10 ml distilled water.

Solutions A and B were poured together in a separating funnel with 10 ml benzene, then hydrochloric acid diluted in 1 : 1 ratio was added to the mixture till the discoloration of aqueous phase. The mixture was shaken and after distribution the iodine containing benzene-phase was separated from the aqueous phase.

1 g of the grease to be labelled had been added to the iodine solution and kept in darkness for 48 hours. After the completion of iodizing the excess of iodine was removed by shaking with aqueous thiosulphate solution after the benzene phase was dried (e. g. by silica gel, sodium sulphate) and benzene was distilled at a low pressure.

In case the solution was not properly cleaned of free iodine the labelled compound caused corrosion on the testing iron plates. Examining the effects of different factors it can be stated that corrosion is caused by free iodine (mainly if traces of water are present). Adequately cleaned and dried linseed oil and oleic acid do not cause corrosion even in 48 hours.

As linseed oil is not a homogeneous compound but a mixture of several glycerides and in addition this chemical heterogeneity is increased by iodizing, the question is raised whether the iodized linseed oil can be regarded as a ho-

mogeneous substance in different degreasing processes, i. e. it can be used as a radioindicator.

To settle these problems different tests were carried out.

### Solvent degreasing of steel surface contaminated with marked linseed oil

A steel sample of known surface was tested with iodized linseed oil and the activity of grease contamination was measured. Afterwards the sample was put into a solvent, the length of time was so chosen that small a part of grease to be measured by weight should remain on the surface. Taking the partially degreased sample out of the solvent the specific activity of the remaining grease (i. e. the ratio of the count number and weight) was measured after the evaporation of the solvent. The procedure was repeated several times.

The measuring data of the tests carried out in different solvents are given in Tables III—IV—V. When dissolving in benzene (2 ml/cm<sup>2</sup>) the iodized material the specific activity remained practically the same during the dissolving tests (Table III).

Table III

Dissolving of linseed oil marked with iodized linseed oil in benzene.  
(Amount of the applied solvent 2 ml/cm<sup>2</sup> surface)

Time of dissolving sec	Grease impurity		Measured activity cpm	Specific activity cpm/1 g
	surface g/12.3 cm <sup>2</sup>	weight g/cm <sup>2</sup>		
0	0.0486	$3.98 \cdot 10^{-3}$	504.020	$10.3 \cdot 10^5$
10	0.0410	$3.36 \cdot 10^{-3}$	437.545	$10.7 \cdot 10^6$
25	0.0165	$1.35 \cdot 10^{-3}$	174.710	$10.6 \cdot 10^6$
35	0.0074	$6.06 \cdot 10^{-4}$	77.021	$10.4 \cdot 10^6$

Table IV

Dissolving of linseed oil marked with iodized linseed oil in carbon tetrachloride.  
(Amount of the applied solvent 2 ml/cm<sup>2</sup> surface)

Time of dissolving sec	Grease impurity		Measured activity cpm	Specific activity cpm/1 g
	surface g/12.3 cm <sup>2</sup>	weight g/cm <sup>2</sup>		
0	0.0302	$2.47 \cdot 10^{-3}$	350.000	$11.6 \cdot 10^6$
10	0.0070	$5.74 \cdot 10^{-4}$	93.800	$12.4 \cdot 10^6$
20	0.0016	$1.31 \cdot 10^{-4}$	19.700	$12.3 \cdot 10^6$

Table V

Dissolving of linseed oil marked with iodized linseed oil in carbon tetrachloride.  
(Amount of the applied solvent 4 ml/cm<sup>2</sup> surface)

Time of dissolving sec	Grease impurity		Measured activity cpm	Specific activity cpm/l g
	surface g/12.2 cm <sup>2</sup>	weight g/cm <sup>2</sup>		
0	0.1401	$1.15 \cdot 10^{-2}$	1,248,000	$8.9 \cdot 10^6$
5	0.0316	$2.59 \cdot 10^{-3}$	278.299	$8.8 \cdot 10^6$
10	0.0148	$1.215 \cdot 10^{-3}$	137.248	$9.3 \cdot 10^6$
25	0.0006	$4.91 \cdot 10^{-5}$	5.400	$9.0 \cdot 10^6$

The dissolving of iodized linseed oil took place in carbon tetrachloride of 2 ml/cm<sup>2</sup> and 4 ml/cm<sup>2</sup> quantities without using mechanical effect. From the measuring data the specific activity of labelled linseed oil appears to be constant within an error of  $\pm 10\%$ .

It was examined, whether the labelled linseed oil mixed into vaseline or paraffin is a suitable tracer. The dissolving tests were performed in 1.2 ml/cm<sup>2</sup> carbon tetrachloride. The results of the measurements are shown in Tables VI, VII and it can be established, that the tracer proved to be a good indicator under this circumstance too.

#### Alkali degreasing of steel surface contaminated with labelled linseed oil

The behaviour of vaseline and paraffine, mixed with labelled linseed oil and that of the radio-indicator — linseed oil with I-131 isotope alone — were also examined when degreasing in an alkali bath. The volume of the bath was 8 ml/cm<sup>2</sup> and the temperature 80–90 °C.

The results are presented in Tables VIII, X and XI

Table VI

Dissolving of vaseline marked with iodized linseed oil in carbon tetrachloride. (Amount of the applied solvent 1.2 ml/cm<sup>2</sup> surface)

Time of dissolving sec	Grease impurity		Measured activity cpm	Specific activity cpm/l g
	surface g/12.2 cm <sup>2</sup>	weight g/cm <sup>2</sup>		
0	0.0214	$1.75 \cdot 10^{-3}$	44.614	$2.08 \cdot 10^6$
10	0.0169	$1.39 \cdot 10^{-3}$	35.200	$2.08 \cdot 10^6$
20	0.0111	$9.10 \cdot 10^{-4}$	25.484	$2.32 \cdot 10^6$
30	0.0058	$4.76 \cdot 10^{-4}$	16.005	$2.76 \cdot 10^6$



Table VII

Dissolving of paraffin marked with iodized linseed oil in carbon tetrachloride.  
(Amount of the applied solvent 1.2 ml/cm<sup>2</sup> surface)

Time of dissolving sec	Grease impurity		Measured activity cpm	Specific activity cpm/1 g
	surface g/12.2 cm <sup>2</sup>	weight g/cm <sup>2</sup>		
0	0.0715	$5.86 \cdot 10^{-3}$	167.257	$2.34 \cdot 10^6$
10	0.0647	$5.22 \cdot 10^{-3}$	141.481	$2.19 \cdot 10^6$
20	0.0506	$4.15 \cdot 10^{-3}$	118.170	$2.34 \cdot 10^6$
30	0.0380	$3.12 \cdot 10^{-3}$	81.121	$2.14 \cdot 10^6$
90	0.0058	$0.48 \cdot 10^{-3}$	14.641	$2.52 \cdot 10^6$

Table VIII

Removing of linseed oil marked with iodized linseed oil in alkali degreasing bath.  
(Volume of the applied bath 8 ml/cm<sup>2</sup> surface, temperature 80° C)

Time of dissolving sec	Grease impurity		Measured activity cpm	Specific activity cpm/1 g
	surface g/12.2 cm <sup>2</sup>	weight g/cm <sup>2</sup>		
0	0.0173	$1.42 \cdot 10^{-3}$	74.795	$4.32 \cdot 10^6$
10	0.0166	$1.36 \cdot 10^{-3}$	73.578	$4.44 \cdot 10^6$
40	0.0154	$1.26 \cdot 10^{-3}$	67.292	$4.37 \cdot 10^6$
50	0.0129	$1.06 \cdot 10^{-3}$	57.210	$4.43 \cdot 10^6$
110	0.0126	$1.03 \cdot 10^{-3}$	53.413	$4.25 \cdot 10^6$

Table IX

Removing of vaseline marked with iodized linseed oil in alkali degreasing bath.  
(Volume of the applied bath 16 ml/cm<sup>2</sup> surface, temperature 90° C)

Time of dissolving sec	Grease impurity		Measured activity cpm	Specific activity cpm/1 g
	surface g/12.2 cm <sup>2</sup>	weight g/cm <sup>2</sup>		
0	0.1022	$8.36 \cdot 10^{-3}$	53.069	$5.22 \cdot 10^5$
5	0.0413	$3.38 \cdot 10^{-3}$	21.520	$5.22 \cdot 10^5$
10	0.0299	$2.45 \cdot 10^{-3}$	15.690	$5.25 \cdot 10^5$
20	0.0186	$1.53 \cdot 10^{-3}$	9.550	$5.14 \cdot 10^5$
30	0.0098	$0.80 \cdot 10^{-3}$	5.190	$5.29 \cdot 10^5$

Table X

Removing of paraffin marked with iodized linseed oil in alkali degreasing bath.  
(Volume of the applied bath 8 ml/cm<sup>2</sup> surface, temperature 80° C)

Time of dissolving sec	Grease impurity		Measured activity cpm	Specific activity cpm/1g
	surface g/12.2 cm <sup>2</sup>	weight g/cm <sup>2</sup>		
0	0.0642	$5.26 \cdot 10^{-3}$	85.606	$13.35 \cdot 10^6$
10	0.0608	$4.99 \cdot 10^{-3}$	78.877	$13.00 \cdot 10^6$
20	0.0412	$3.37 \cdot 10^{-3}$	58.500	$14.20 \cdot 10^6$
30	0.0389	$3.19 \cdot 10^{-3}$	52.478	$13.50 \cdot 10^6$
60	0.0343	$2.81 \cdot 10^{-3}$	47.805	$13.90 \cdot 10^6$
16 perc	0.0113	$0.92 \cdot 10^{-3}$	15.215	$13.50 \cdot 10^6$

Table XI

Removing of stearic acid marked with iodized linseed oil in alkali degreasing bath.  
(Volume of the applied bath 8 ml/cm<sup>2</sup> surface, temperature 80° C)

Time of dissolving sec	Grease impurity		Measured activity cpm	Specific activity cpm/1g
	surface g/12.2 cm <sup>2</sup>	weight g/cm <sup>2</sup>		
0	0.1315	$10.8 \cdot 10^{-3}$	108.600	$8.26 \cdot 10^5$
5	0.0650	$5.32 \cdot 10^{-3}$	53.594	$8.26 \cdot 10^5$
15	0.0351	$2.88 \cdot 10^{-3}$	28.965	$8.20 \cdot 10^5$
25	0.0290	$2.38 \cdot 10^{-3}$	24.170	$8.32 \cdot 10^5$

The constancy of the specific activity shows that labelled linseed oil is suitable to follow the effectiveness of degreasing for the case of alkali degreasing too.

In the alkali degreasing process the remaining vaseline or paraffine and that mixed into linseed oil take place at a constant ratio.

The possibility of tracing stearic acid by iodized linseed oil was also examined. Though the behaviour of stearic acid can be reliably sought for by C-14 marking in case of thin layers, tracing with iodine is more suitable when thicker layers of stearic acid are present. In the course of degreasing the specific activities practically do not change so stearic acid too can be traced in this way (Table XI).

## Further possibilities of radioindication tracing

### *Zn-65 isotope containing Zinc-stearate as tracer*

Starting out from the fact, that among grease impurities metal-soaps can also be found (e. g. Ca-stearate, Pb-stearate and Al-stearate) an attempt was made to apply  $^{55}\text{Zn}$ -stearate for tracing greases.

From among the feasible metal soaps the zinc stearate was chosen because the Zn-65 isotope is advantageous for measuring. Its half-life is 250 days, it emanates a well-detectable gamma radiation of 1.11 MeV, which can be measured with suitable efficacy by NaI(Tl) scintillator.

#### Production of Zn-stearate:

After having tried several methods found in the literature [5], marked Zn-stearate was obtained as follows.

2 g alkali-soap was dissolved in a mixture of 10 ml 95% ethyl-alcohol and 150 ml water. Zn-acetate taken in 3—5% excess over the stoichiometric quantity was dissolved in 30 ml water. While continually stirring, the solution was slowly added to the alkali soap solution. After standing for six hour the precipitate was filtered, then washed with distilled water and alcohol and rinsed with ether. The Zn-soap was dried in an exsiccator at 45 °C.

According to preliminary experiments the  $^{55}\text{Zn}$ -stearate could be used as a tracer. Detailed results will be given in a following paper.

### *Triphenyl-antimony as a tracer*

The triphenyl-Sb-124 is soluble in grease thus it can be mixed as an indicator into the grease to be traced. According to the results of the experiments it is a suitable tracer, but its production is considerably more complicated and difficult than that of the compounds labelled with iodine.

### *Activation of abrasive masses*

An attempt was made to trace the "brown" and "white" abrasive masses used in practice by direct activation. For this purpose samples of the abrasive masses were activated for 48 hours in a reactor. The masses became active (i. e. iron, chrome etc.) but at the same time — probably because of polymerization they were transformed into spongy materials insoluble in oils and grease-solvents, so they could not be used for degreasing tests.

### *Tracing of the thickness of a grease layer by cementation*

Experiments were made in connection with "posttracing" of thin grease-layers remained after degreasing. The reason of these tests was that these might be a possibility to control the work between the manufacturing pro-

cesses in a factory. The basis of these tests was the assumption that the grease layer remaining on the metal iron surface would prevent the copper — i. e. silver — ion from cementation as a function of its thickness.

The application of silver cementation is justified by radioisotope measuring technical reasons. Ag-110 has a half-life of 270 days its beta-radiation is accompanied by gamma-ray thus it is well measurable by using a scintillation method. Because of the passivating effect of nitrate-ions the tests were performed in saturated silver sulphate solution.

The cementation experiments by active silver were begun by clearing up the question of reproducibility. The experiments were made as follows.

$^{110}\text{AgNO}_3$  solution of 0.5 mg/ml was added to a  $\text{Ag}_2\text{SO}_4$  solution of 0.4 g/100 ml at 20 °C. Simultaneously 5 pieces of electrolytically degreased steel plates of 12.2 cm<sup>2</sup> surface were immersed in the solution for 30 seconds. Then the activity of the thin silver layer cemented to the surface of the plate was measured. The average activities (based on five-five measurements each) of the six parallelly investigated plates are given in Table XII.

Table XII  
Cementation of active silver

Number of plate	Activity (cpm)	$\Delta n = \frac{\Sigma n}{5} - n$
1	5224	-77
2	4921	+226
3	5338	-193
4	5330	-185
5	4921	+224

After having obtained satisfying result in conjunction with reproducibility, the relationship between cementation and the thickness of the layer was investigated. The informative tests were made as follows:

Plates of the same purity were plunged into benzene solutions of different oil concentrations. After the evaporation of the solvent active silver was cemented and the activity of the silver layer was measured. In the same manner several grease layers of different thicknesses were applied using stearic acid dissolved in ether. The results are presented in Tables XIII—XIV.

From these results it appears (apart from some divergent results probably caused by experimental errors), that there is a relationship between the thickness of the grease layer and the quantity of the cemented silver. To improve the method and to elucidate its applicability further thorough investigation of the mechanism of silver cementation is needed.

**Table XIII**  
Cementation of active silver

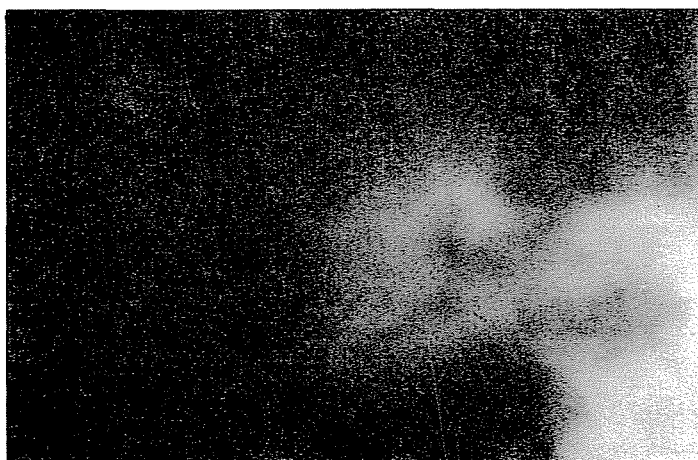
Thickness m $\mu$	Activity of Ag <sup>+</sup> layer cpm
Electrolytic degreased plate	5.500
1.25	2.600
2.50	3.200
5.00	1.500
10.00	2.000
20.00	1.200

**Table XIV**  
Cementation of active silver

Applied linseed oil layer	Activity
1.5 m $\mu$	13.800 cpm
3.75 ..	16.500 ..
7.5 ..	15.100 ..
15.0 ..	9.800 ..

#### *Autoradiographic investigation*

Attempts were made to study the distributions of thin grease layers by autoradiograms. In this manner it could be established whether the grease is spread uniformly or in "islets" (*Fig. 1*).



*Fig. 1*

Table XV

Following the course of solvent (benzene) and electrolytic degreasing at linseed oil impurity marked with iodized (I-131) linseed oil

Number of measurements	Time of degreasing (sec)	Grease remaining on the surface $\mu\text{g}/\text{cm}^2$	Dissolved grease $\mu\text{g}/\text{cm}^2$	Activity of the grease on the surface	Grease contamination of the solvent g/100 ml solvent
Degreasing: in 2.05 ml/cm <sup>2</sup> benzene					
1.	Initial Impurity	3980	—	504.020	0.00
2.	10	3360	620	437.545	0.03
3.	25	1350	2010	174.710	0.13
4.	35	606	744	77.010	0.17
5.	10	377	229	62.152	0.00
6.	70	8.20	368.80	1.263	0.03
7.	130	6.56	1.64	1.105	0.03
8.	190	6.56	0.00	1.109	0.03
9.	120	2.84	3.72	900	0.00
Degreasing: electrolytic					
10.	60	1.57	1.27	500	
11.	150	0.315	1.255	103	

The radiogram shows the distribution of the grease on the surface of the plate contaminated with iodized linseed oil in an intermediary phase of solvent degreasing.

On the picture the cleansed surface is black, while the white mottles indicate the presence of grease. As it can be seen the grease layer remaining on the surface after dissolving is not uniform. The average surface density of the grease layer is  $10^{-2}$  g/cm<sup>2</sup>.

#### *Investigation of the effectiveness of degreasing with marked grease*

The effectiveness of electrolytic degreasing method was studied with a I-131 isotope containing linseed oil.

Steel plates of  $3.5 \times 3.5$  mm were contaminated with marked linseed oil. These plates were first degreased in solvent, then electrolytically. In case of solvent degreasing it was determined by measuring the activity of the radio-

Table XVI

Following the course of solvent (carbon tetrachloride) and electrolytic degreasing at linseed oil impurity marked with iodized (I-131) linseed oil

Number of measurements	Time of degreasing (sec)	Grease remaining on the surface $\mu\text{g}/\text{cm}^2$	Dissolved grease $\mu\text{g}/\text{cm}^2$	Activity of the grease on the surface	Grease contamination of the solvent g/100 ml solvent
Degreasing: in 2.05 ml/cm <sup>2</sup> carbon tetrachloride					
1.	Initial Impurity	2470	—	350.100	0.00
2.	10	574	1.896	93.800	0.094
3.	20	131	443	19.700	0.117
4.	30	37.7	93.3	6.050	0.121
5.	40	19.8	17.9	3.150	0.122
6.	50	13.1	6.7	2.130	0.122
7.	60	12.6	0.5	2.018	0.122
8.	70	12.6	6.3	1.015	0.123
9.	170	6.3	6.3	1.625	0.123
10.	10	3.77	2.53	1.205	0.00
11.	20	3.77	0.00	1.200	0.00
12.	80	3.48	0.29	1.100	0.00
Electrolytic degreasing					
13.	90	0.63	1.85	208	

indicator at established intervals how much grease remained on the surface. Mechanical effect was not applied and in the course of the experiments practically pure solvents were used. After solvent degreasing, electrolytic degreasing was applied.

Dissolving tests were carried out also with C-14 containing stearic acid in agreement with the aforementioned method.

The results are presented in Tables XV—XIX.

The presented results wish to justify that the degreasing process can be successfully followed. The behaviour of stearic acid labelled with C-14 isotope and that of linseed oil labelled with J-131 isotope were similar in the course of degreasing, the iodized product can be conveniently detected also in case of greater grease-thickness.

Table XVII

Following the course of solvent (carbon tetrachloride) and electrolytic degreasing at linseed oil impurity marked with iodized (I-131) linseed oil. (With greater initial impurity, than in Table XVI.)

Number of measurements	Time of degreasing (sec)	Grease remaining on the surface $\mu\text{g}/\text{cm}^2$	Dissolved grease $\mu\text{g}/\text{cm}^2$	Activity of the grease on the surface	Grease contamination of the solvent g/400 ml solvent
Degreasing: in 4.1 ml/cm <sup>2</sup> carbon tetrachloride					
1.	0	1,150.000		1,248.000	0
2.	5	2.590	1,147.410	278.299	28.68
3.	10	1.215	1.375	137.248	28.72
4.	25	49.1	1.165.9	5.400	
5.	35	33.9	15.2	3.742	
6.	45	24.6	9.3	2.722	
7.	55	12.3	12.3	2.720	
8.	65	12.3	—	2.720	
9.	75	12.3	—	2.700	
10.	135	12.3	—	2.700	
11.	195	12.3	—	2.690	
12.	255	11.9	0.4	2.618	28.75
13.	10	8.44	3.46	1.877	0.00
14.	70	7.45	0.99	1.646	0.00
15.	130	7.30	0.15	1.615	0.00
16.	10	7.25	0.05	1.605	0.00
17.	70	7.25	—	1.610	0.00
18.	5	7.25	—	1.599	0.00
19.	10	7.25	—	1.580	0.00
Electrolytic degreasing					
20.	15	2.18	5.07	484	
21.	75	1.05	1.13	231	



Table XVIII

Following the course of solvent (carbon tetrachlorid) degreasing at C-14 marked stearic acid impurity

Number of measurings	Time of degreasing (sec)	Grease remaining on the surface $\mu\text{g}/\text{cm}^2 \cdot 10$	Dissolved grease $\mu\text{g}/\text{cm}^2 \cdot 10$	Activity of the grease on the surface	Grease contamination of the solvent g/100 ml solvent
Degreasing: 2 ml/cm <sup>2</sup> carbon tetrachlorid					
1.	Initial impurity	45.5		83.100	0
2.	7	36.3	9.2	66.200	$1 \cdot 10^{-5}$
3.	14 mechanical effect	8.6	27.7	15.680	$1 \cdot 10^{-5}$
4.	21	8.05	0.55	14.700	$1 \cdot 10^{-5}$
5.	24 hours	4.0	4.05	3.660	0
Degreasing: 2 ml/cm <sup>2</sup> carbon tetrachlorid					
1.	Initial impurity	89.0		163.000	0
2.	7	89.0		163.000	$1 \cdot 10^{-5}$
3.	14 mechanical effect	11.10	77.9	20.250	$1 \cdot 10^{-5}$
4.	21	7.23	3.87	13.200	$1 \cdot 10^{-5}$
5.	28 mechanical effect	5.93	1.30	10.800	$1 \cdot 10^{-5}$
6.	24 hours	2.02	3.91	3.690	0

Table XIX

Following the course of solvent (benzene) and electrolytic degreasing at C-14 marked stearic acid impurity

Number of measurings	Time of degreasing (sec)	Grease remaining on the surface $\mu\text{g}/\text{cm}^2 \cdot 10$	Dissolved grease $\mu\text{g}/\text{cm}^2 \cdot 10$	Activity of the grease on the surface	Grease contamination of the solvent g/100 ml solvent
Degreasing: in 2 ml/cm <sup>2</sup> benzene					
1.	Initial impurity	34.00		62.000	0
2.	7	28.70	5.30	52.500	$1 \cdot 10^{-5}$
3.	14	6.38	22.32	11.640	$1 \cdot 10^{-5}$
	mechanical effect				
4.	21	6.30	0.08	11.510	$1 \cdot 10^{-5}$
5.	24 hours	3.18	3.12	5.800	0
Electrolytic degreasing					
	30 sec	1.47	1.71	2.580	
Degreasing: in 2 ml/cm <sup>2</sup> benzene					
1.	Initial impurity	66.2		121.000	0
2.	7	58.8	7.4	96.200	$1 \cdot 10^{-5}$
3.	14	11.1	47.7	20.200	$1 \cdot 10^{-5}$
	mechanical effect				
4.	21	10.60	0.5	19.350	$1 \cdot 10^{-5}$
5.	28	6.28	4.32	11.440	$1 \cdot 10^{-5}$
	mechanical effect				
6.	24 hours	5.05	1.23	9.290	0
Electrolytic degreasing					
7.	60 sec	0.87	4.18	1.590	

### Summary

According to the experiments made hitherto it can be stated, that the tracing of unsaturated oils with active iodine (I-131) is a useful, simple method which can easily and suitably be carried out for following the effectiveness of degreasing.

Advantages: it is a cheap, well-detectable indicator that can be produced in common isotope laboratories.

Disadvantages: on account of the decay of iodine during a longer series of experiments its reproduction must be several times repeated.

The moisture content and free iodine make the indicator considerably aggressive, therefore it can be applied only after thorough clearing.

The use of C-14 containing oils is also a suitable method, but these can be produced only in special laboratories and they are expensive compared with iodine. The measuring of C-14 needs special methods and its determination with gas flow GM tube is rather uncertain even in the case when considering self-absorption.

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