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THE MEANING OF TRIBOCHEMICAL REACTIONS BETWEEN ADDITIVES AND METALS DURING FRICTION AND WEAR PROCESSES

Helga Dunken

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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by

H. Dunken

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13. ABSTRACT

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This article concerns the meaning of tribochemical reactions between additives and metals during friction and wear process. [AP1200863]

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THE MEANING OF TRIBOCHEMICAL REACTIONS BETWEEN ADDITIVES AND METALS DURING FRICTION AND WEAR PROCESSES

[Article by Helga Dunker, Chemistry Section of Friedrich Schiller University, Jena, Surface Chemistry Research Group, Zeitschrift Fuer Chemie, German, Vol 11, No 6, 1971, pp 213-219]

1. Introduction

Wear and fatigue phenomena connected with friction processes cause enormous damages to machine and tool parts [1]. To reduce the damages friction endangered parts are lubricated.

Selection of suitable lubrication media for the various mechanical stresses takes place even today by more or less trial and error.

The lubricating media in general have to fulfill several functions. The following considerations are limited to the area of solid body or boundary friction. This area determined considerably through the energetic interact of the atoms or molecules respectively of the boundary phas . The molecules of the lubricant medium cause the so-call boundary lubrication in this area which is supposed to decrease boundary friction.

Boundary friction and lubrication are important to all metal parts which move mechanically against each other (gears, bearings, pistons, and so on) and which are not separated from each other through a sufficiently thick liquid or gas layer with hydrodynamic lubricating effect. The transition from boundary friction to internal friction is not clearly defined. Frequently, the friction coefficient μ is considered a measure of it. Fig. 1 shows schematically the changes of the friction coefficient with increasing layer

thickness of the phase between the metal surfaces. Phenomenologic description of the friction and tangential shearing force K_R is carried out by the Coulomb-Amonton law:

$$K_R = \mu K_n + a,$$

a is the parameter which covers the properties which are specific to the boundary surface; or better with a statement by Derjagin [2]:

$$K_R = \mu[K_n + K_h]$$

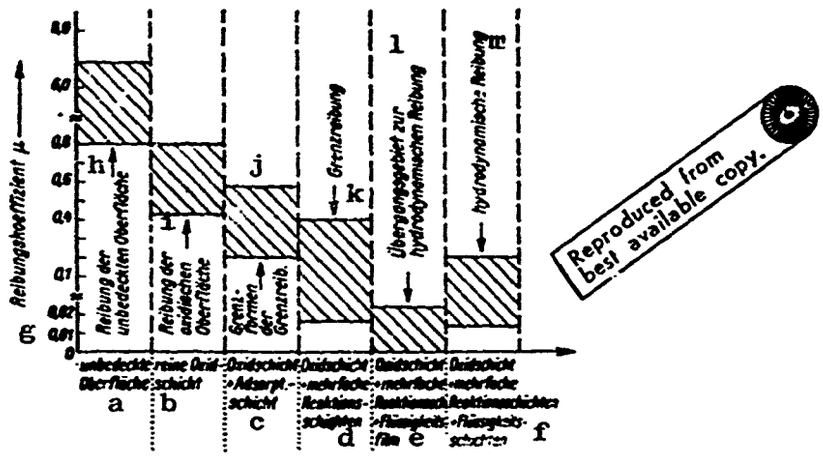

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Fig. 1. Schematic Representation of the Dependence of the Friction Coefficient μ from the Layer Thickness of the Boundary Phase [3].

Key:

a. Uncovered surface
b. Pure oxide layer
c. Oxide layer + adsorption layer
d. Oxide layer + multiple reaction layers
e. Oxide layer + multiple reaction layers + liquid film
f. Oxide layer + multiple reaction layers + liquid layers
g. Friction coefficient, μ
h. Friction of the uncovered surface
i. Friction of the oxidic surface
j. Boundary forms of boundary friction
k. Boundary friction
l. Transition region to hydrodynamic friction
m. Hydrodynamic friction

which covers the adhesive force K_h which is caused by the molecular roughness of the surface. According to Derjagin the effective touching surfaces between the two solid bodies and the specific interlinking between them enter into K_h.

In rough approximation the tangential shear force is directly proportional to the normal force K_n, which in effect is perpendicular to the transverse direction. There is a series of additional statements which are not listed here, and which give more detailed description for special cases. We point out the monographs by Achmatov [3] on boundary friction and by Rehbinder, Lichtman and Karpenko on the deformation of metals in the presence of boundary surface a[illegible] materials [4]. In these statements specific molecular effects are only covered globally by the adhesive friction coefficient and the adhesive force. Surely, the real stress on metals in bearings, during drawing or turning is described by these equations. Rehbinder [4] is justified in pointing out volume forming and plastic deformation during friction processes.

Two problems make a consequential theoretical description of friction and wear processes difficult:

1. The real processes in machines and transmissions cannot be simulated simply by model experiments.

2. Molecular concepts on boundary friction are deduced frequently from macroscopic parameters such as wear magnitudes, hardness, adhesive friction coefficients, or correlated with them without taking into consideration that macroscopic magnitudes frequently describe several molecular effects which are working in opposite directions.

Until now no complete theory on friction or wear phenomena exists which would permit in any case a prediction of suitable lubricating media or the pairing of raw materials.

With reference to the effect named after him, Rehbinder [4] emphasized the role of adsorption of boundary active substances on deformation and forming phenomena of metals. According to this, adsorbed molecules diffuse on the metal surface and "creep" into micro cracks. The adsorbate connection also weakens the metal-metal bonding in the metallic boundary area. These two effects are responsible for easier formability. Many papers of this school [4] investigated above all tribophysical changes of the metal surface and the lower lying layers. It is striking in these papers that air

or oxygen and paraffin oils as well are not considered to be boundary area active. According to Bowden and Tabor [5] the high temperatures at the direct points of contact of the metal boundary areas, so-called "hot spots," are responsible for welding and increase of the friction force. These authors, moreover, view the importance of adsorption in preventing the immediate metallic contact through adsorptive protective layers. Active lubrication media should build up such a protective layer which is bound to energy maxima connected with high temperatures. High pressure additives (called also EP-additives, EP ≙ extreme pressure) which preponderantly become effective in the boundary layer according to present concepts are required to

1. Decompose upon greater stress into reactive fragments which react with the metal atoms at the areas of contact;

2. Form a temperature stable protective layer which also decreases adhesive friction;

3. Remove roughness of the metal surface through directed corrosive attack and thus prevent temperature maxima.

Tribochemical reactions are taken into consideration very little in both concepts discussed. In 1930 Fink [6] in his works on friction oxidation recognized the importance of tribochemical processes at metal areas under mechanical stress.

Work on materials stressed by friction carried out by Thiessen, Meyer, and Heinicke [7] has laid the foundation and contributed decisively to the development of tribochemistry.

2. Some Principles of Tribochemistry and Tribocorrosion

With each mechanical stressing of a metal free energy ΔF, in the thermodynamics sense is introduced into the system. This free energy can be stored potentially in the metal surface through the formation of dislocations and defects. Fig. 2 shows schematically the impact of a sphere model on a metal surface. Lattice disturbances also extend to lower atom positions. This stored free energy and also the "timely" free energy can force chemical reactions between the metal atoms and the molecules and the surrounding medium which would not take place under normal conditions.

Temperature independence of the speed of reaction is a further essential characteristic of tribochemical reactions. The activation energy is introduced as free energy.

Finally, tribochemical reactions depend strongly on the kind of processing and then on the energy supply.

More recent findings on tribochemical reactions have led to further aspects of wear processes. For a number of years the field of tribocorrosion has been investigated by several groups. The paper by Heinicke and Harenz [8] provides a certain summary.

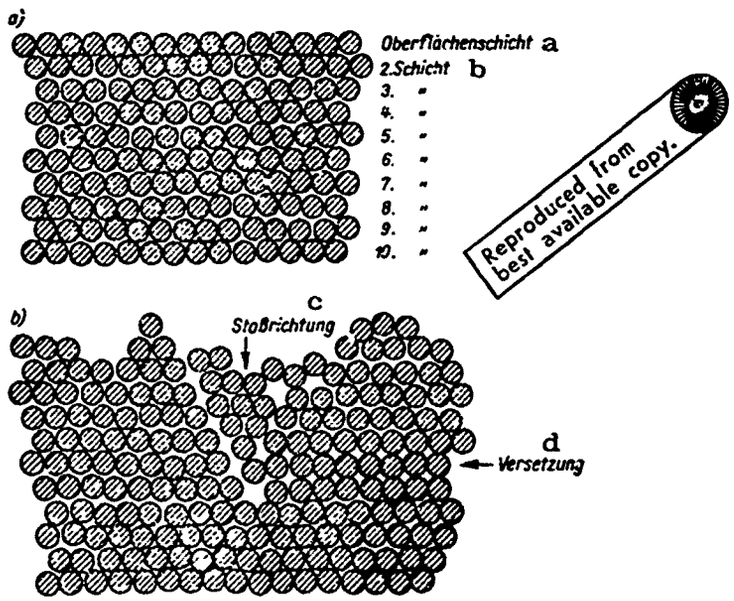

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Fig. 2. Schematic Representation of Disturbances in the Lattice of an Ideal Crystal (a) and after an Impact (b)

Key:

a. Surface layer
b. Layer
c. Direction of impact
d. Dislocation

Very directed experiments on various machine parts under mechanical stress enabled Heinemann [9] to prove that tribocorrosion leads to considerable wear damage on the metals which are of the order of magnitude of grinding or turning wear forms. Fig. 3 shows a summary from this paper.

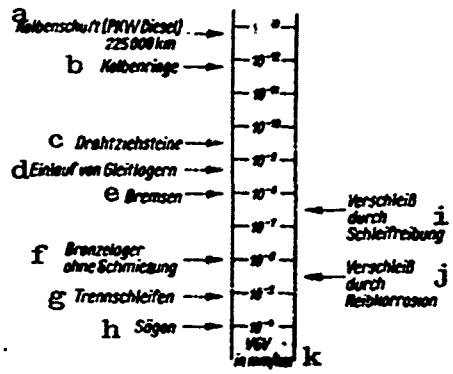

Fig. 3. Schematic Representation of the Wear-gliding Path Ratio (WGR) at Different Mechanical Stresses in Practice [9]

Key:

a. Piston shaft (diesel driven sedan)
b. Piston rings
c. Wire pulley and weight
d. Breaking in of plain bearings
e. Brakes
f. Bronze bearings without lubrication
g. Separation grinding
h. Sawing
i. Wear through grinding friction
j. Wear through rubbing corrosion
k. Wear-gliding path ration (WGR) in mm/km

It represents the ratio of wear depth in mm to path of gliding in km.

Tribooxidation plays a special role in tribocorrosive phenomena; it occurs always if working takes place under atmospheric conditions. The experiments by Fink [10] show unequivocally that abrasion as a measure of wear is considerably less in an inert gas atmosphere than in air. Here abrasion is defined as follows:

$$A = \Delta m = m_v - m_n$$

$$a = \frac{\Delta m}{m_v}$$

a = specific abrasion, m_v mass of the metal before, m_n mass of the metal after working.

All experimental results on tribocorrosion agree that tribochemical reactions are connected with plastic deformation of the surface and lower lying layers.

From the work done to date the following essential processes during mechanical working of metallic boundary areas with influence on the wear behavior can be given as a summary:

1. Adsorption or chain sorption, respectively, of boundary-area-active materials at the area being machined;

2. Boundary-area-active materials according to Rehbinder facilitate plastic forming of metals;

3. According to Heinicke [11] tribochemical reactions with established tribosorption lead to structure changes in the boundary layer and can cause considerable corrosive damage;

4. High energy densities and connected with this high temperatures at metallic micro regions lead to chemical reactions and thus to considerable changes of the boundary phase.

3. The Effect of Additives on Metal Surfaces

Experimental investigations to determine the working mechanism of additives at metallic boundary areas can be divided into three groups:

1. Experiments which take place under very realistic dynamic conditions (transmission tests, test bench experiments). They only test the effect of additives phenomenologically. These experiments are very time consuming and expensive.

2. Semitechnical dynamic experiments with model systems and fixtures which simulate the essential aspects of the true mechanical stress (four ball apparatus, scratch test, and so on). With these experiments load parameters can be correlated with changes at the metal surface and in the liquid phase.

3. Static experiments which essentially cover molecular phenomena and changes of state at the phase boundary areas but do not permit conclusions with

respect to dynamic, machining experimental conditions. Among these are measurements of the adhesion-friction-coefficient, adsorption investigations with various methods, hot-wire-methods (the reaction products are analyzed at a heated wire immersed into the liquid phase, and sometimes conductivity measurements are also carried out).

In the evaluation of the experimental results the task consists of correctly attributing molecular parameters to macroscopic measuring magnitudes. For all experiments on the effect mechanism of additives it is important that all reaction possibilities are taken into consideration. Many additive tests are lacking because the influence of the basic oil as the solvent, respectively, is given little attention.

Koenig [12] was able to prove in our laboratories what importance is due the interaction of aliphatic and aromatic hydrocarbons with metal surfaces. He investigated in model experiments where slipping-off and impact processes simulated mechanical working of metals, the abrasion behavior of the metals iron, cobalt, nickel, and copper against benzene, cyclohexane, n-hexane and cetane as a measure of wear. Gas, liquid, and solid phases were analyzed by various methods after the working.

Fig. 4 shows a few abrasion values. The clear differences of abrasion values from experiments in air and under inert conditions are remarkable.

During working a series of different reaction products is formed. Table 1 shows analyzed reaction products for selected systems.

The results were confirmed by tribochemical reactions with gaseous hydrocarbons carried out by Heinicke and coworkers [13]. Koenig was able to prove unequivocal relations between adsorption reactions of the hydrocarbons and the wear behavior of corresponding systems.

1. Adsorption is determined substantially by the properties of metal and hydrocarbon. In a vacuum, saturated hydrocarbons are adsorbed dissociatively [14], [15] and aromatics associatively [16]. In the first case σ-C-Me bonds are formed which are very stable thermally. At higher temperatures the associative sorption structures which are based on π-bonds mostly change over into dissociative forms which are stabilized through σ-bonds, with this hydrogen is liberated.

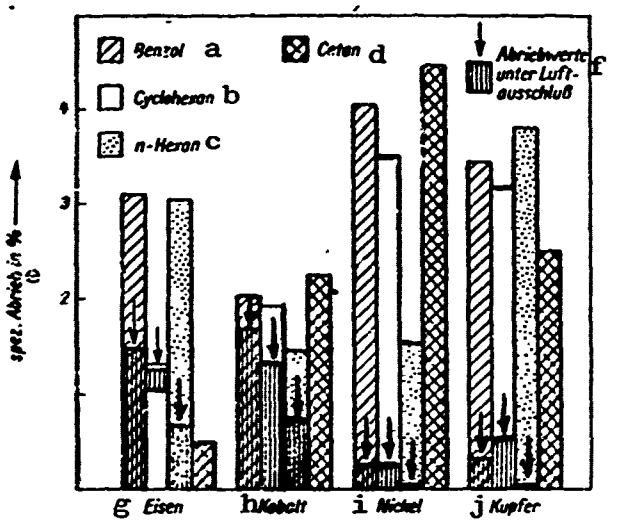

Fig. 4. Representation of Specific Wear for Various Metals During Working in Liquid Hydrocarbons in the Presence and Absence of Air; Time of Working 500 h.

Key:

a. Benzene
b. Cyclohexane
c. N-hexane
d. Cetane
e. Specific abrasions in %
f. Abrasion values in absence of air
g. Iron
h. Cobalt
i. Nickel
j. Copper

2. In the presence of atmospheric oxygen, oxidic surface layers form where aromatics are adsorbed preferentially. However, the adsorbate layers being formed are not very stable energetically.

3. Wear behavior is determined by metal hardness only secondarily. Above all the sheer strength of the adsorbate layers is responsible for the extent of abrasion. Here, oxidic layers possess less strength and thus yield higher abrasion.

4. For abrasion of metals in the presence of hydrocarbons under atmospheric oxygen solubility in

Table 1

System	Reaction Products in the Gas and Liquid Phase
Fe/Benzene/air	CO_2; traces of CH_4, C_2H_4, C_6H_{12}
Fe/Hexane/air	H_2; little C_6H_{12}; carbonic acids and soaps
Fe/Hexane/no air	Much H_2; trace of; benzene, cyclohexane
Co/benzene	Methane, traces of ethane and propane, cyclohexane
Co/cetane/air	Methane; little ethane, propane and benzene
Co/benzene/no air	Methane, ethane, propane, butane is small quantities
Co/cyclohexane	Much H_2; methane, propane, butane
Cu/benzene/air	No products except CuO and Cu_2O
Cu/cyclohexane/air	Traces of benzene and n-hexane
Cu/hexane/no air	H_2; methane, ethane, ethylene

the hydrocarbon given is responsible as well. This decreases in the systems investigated as the series hexane > cyclohexane > benzene > cetane.

5. According to Koenig [12] mechanical working does not lead to tribochemical equilibrium (working time 500 h). However, with increasing duration of working surface hardening was observed. Fig. 5 shows a comparison between the abrasion-time-curves and the microhardness time-curves. An increase in hardness of the boundary phase with increasing duration of working was observed also by Rehbinder [4] and Neukirchner [17] in other systems.

The model of interaction of hydrocarbons with worked metal surfaces developed by Koenig, permits the interpretation of the semitechnical experiments by Appeldoorn and Tao [18] in the four-ball-instrument, and is in agreement with work by Vinogradov [19]. From these experiments, one can

deduce with great certainty that hydrocarbons are not inert with respect to mechanically stressed metal surfaces, that extended working time will lead to a change of the base oil composition due to tribochemical reactions.

Additives are introduced into base oils only in amounts of 0.5 to 3% by weight. After representing the results for base oil substances ideas on possible effect mechanisms will be developed with the example of sulfur containing additives.

Various EP effective additives with bonded sulfur are known from patent literature. The spectrum of these compounds extends from elementary sulfur to mercaptans, disulfides, polysulfides, thio acids and their derivatives, xanthates and to halogen or phosphorus-containing culsur compounds. The compound classes mentioned last can be loaded especially well because here synergistic effects of the element pairings sulfur-halogen or sulfur-phosphorus, respectively occur.

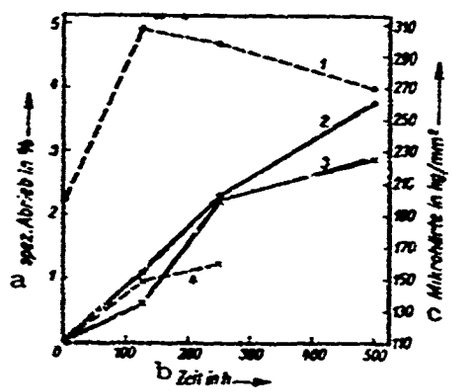

Fig. 5. Dependence of Wear and Surface Hardness (measured by an impression Procedure) to Duration of Working: 1. Microhardness Nickel Cyclohexane/air. 2. Wear Nickel/cyclohexane/air. 3. Wear Copper/Cyclohexane/Air. 4. Microhardness Copper/Cyclohexane/Air

Key:

a. Specific wear in %
b. Time in hours
c. Microhardness in kg/mm^2

From the literature a series of adsorption experiments with sulfur containing compounds and metals are known which show in agreement that these compounds are very boundary-area-active. According to Saleh and coworkers [20], Hobert [21] and Petkow [22] mercaptanes are adsorbed dissociatively, splitting off hydrogen at the same time. This leads to the formation of mercaptide surface compounds. Similar structures were proven by Dilke [23] and Hobert [21] during the interaction with dimethylchioether. The sorption of disulfides on metals also takes place via a mercaptide formation [22]. Besides investigations on glass metal systems there are some experiments with dissolved sulfur compounds. Kuehnel was able to prove irreversible chemisorption of thiophene on Raney - metals [24]. By way of tracer technique, Llopis [25] investigated the adsorption of dimethylthiourea, di- and polysulfides on copper and found the formation of sulfide layers in its course.

Allum and Forbes [26] determined the heats of adsorption of various disulfides. They obtained relatively small values. They explained these results with the formation of mercaptide layers. During static experiments with the hot-wire method disulfide and thioether resulted in sulfidation of the metal surfaces [27] - [32]. As is well known disulfides already decompose at temperatures above 100°C and therefore, as regards these experiments it is not easy to decide whether the primary adsorption step does not start with a thiyl radical [33].

The correlation of these experimental results under static conditions with results obtained during mechanical working is essential for the explanation of the effect mechanism.

Basic work with H_2S and worked metal surfaces were carried out by Meyer and Heinicke [34]. The formation of sulfide layers was followed with radioactive marking and electron microscopic investigations.

Williams [35] proved the formation of iron sulfide from di- or polysulfides in iron friction bearings.

Buechner [36] carried out very extensive static and dynamic investigations on iron samples and di- sulfides as well as alicyclic thio compounds. Labelling the sulfur radioactively he obtained adsorption isotherms for the compounds mentioned which in the region to 100°C led to the conclusion of molecular adsorption layers which transform up to iron sulfide. At higher temperatures adsorption reactions

were observed with decay products of the sulfur compounds. Intermittant impact load as well as the tests in the four-ball-instrument lead to the formation of iron sulfide. Here, adsorption directed, tribochemical reactions could be observed. It was impossible to prove a connection between the area-coverage-density caused by sulfur compounds and the high pressure behavior.

Other authors as well correlated wear behavior and adsorption parameters with smaller loads in the four-ball-instrument. Allum and Forbes found that wear of the steel balls increased if the adsorption heats becomes smaller. At higher loads this correlation was not confirmed [37]. Comparisons between molecular bonding energies and wear parameters are interesting as well. According to literature [38], [39], [37] the following relationships exist. For disulfides and mercaptanes the EP-effectiveness decreases with increasing S-S, or S-C bonding energy respectively. Fig. 6 shows a correlation between S-S bonding energy and the S-R bonding energy in some disulfides put together from literature data. According to this the S-S bonding stability decreases with increasing R-S bonding energy. Through suitable substitution at the organic remainder R-, the S-S bonding force can be varied. The adsorption investigations confirm the influence of the S-S bonding energy on the mercaptide formation.

With the exception of the investigations by Buechner [37], so far all papers on the EP-effectiveness of additives do not pay sufficient attention to tribochemical reactions.

The importance of tribochemical reactions during mechanical working of metals in the presence of sulfur-organic compounds was proven in our laboratory through the work carried out by Wallbraun [40]. During working of compact Ni, Cu, Co, Fe, and Pd samples, stable mercaptide complexes of the general type $[Me(SR)_m]_n$ formed from sec-dibutyl or n-dinonyldisulfide solutions, respectively. In the case of copper the sulfide could be isolated as well.

Figure 7 shows a wear-time curve for some disulfide-metal systems. Increasing wear as a consequence of increasing durations of working confirms the reactivity of these sulfur compounds.

From our investigations the influence of the reaction conditions on wear can be further deduced.

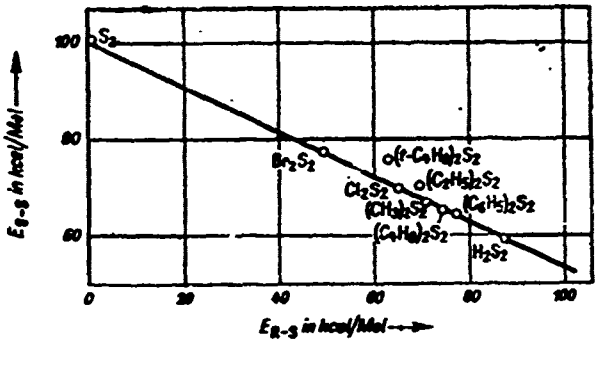

Fig. 6. Connection Between the S-S Bonding Energy E_{S-S}, and the R-S Bonding Energy E_{R-S} in Some Disulfides

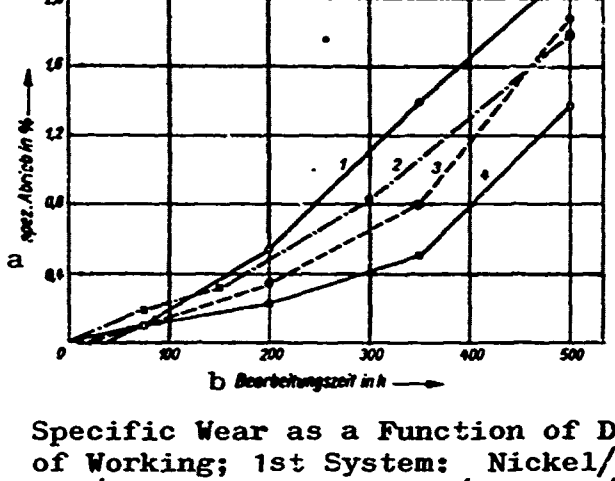

Fig. 7. Specific Wear as a Function of Duration of Working; 1st System: Nickel/0.01 Mol/1 Dibenzyldisulfide/Benzene/No Air. 2nd System: Copper/0.1 Mol/1 p,p'-Dimethyldiphenyldisulfide/1,2-Dichlorethane/Air. 3rd System: Nickel/0.01 Mol/1 Dibenzyldisulfide/Cyclohexane/No air. 4th System: Copper/0.01 Mol/1 Dibenzyl-disulfide/Cyclohexane/Air

Key:

a. Specific wear in %

b. Duration of work in hours

1. As has already been shown for the hydrocarbons, wear increases in general if the experiments were run under the influence of oxygen.

2. The concentration of the boundary area compounds is of considerable influence on the wear values. As can be seen from Fig. 8, wear does not increase monotonously with concentration. Rehbinder was able to prove similar effects with regard to the deformability of the metals in the presence of carboxylic acids and other boundary area active materials [4].

   The wear curves in Fig. 8 cannot be explained solely with adsorption behavior. Very likely two opposing effects are superposed; the decrease of wear in the region of lower concentrations can be due to an adsorption and supply effect, while the increase of wear with increasing concentration might be due to reactive dissolution effects of the boundary layer through the liquid phase. The supply effect is supposed to characterize the phenomenon that the adsorption layer being formed under dynamic reaction conditions is exposed to continuous wear and can form anew only if the diffusion speed of the boundary area active molecules is higher than the speed of wear.

3. The solvent exerts decisive influence on wear. Fig. 9 pictures this influence. Our investigations showed that boundary area active compounds like the sulfur organic substances only slightly shift wear which is due to the solvent. This confirms the thesis that during tribochemical reactions even relatively reaction-inert substances can be converted.

4. In general a temperature increase also increases wear. This result proves indirectly that adsorption reactions which may be temperature dependent take place before the tribochemical reactions.

4. Hypotheses on the Effect Mechanism of Additives

The following reaction steps emerge with priority out of the complexity of phenomena in friction and wear processes:

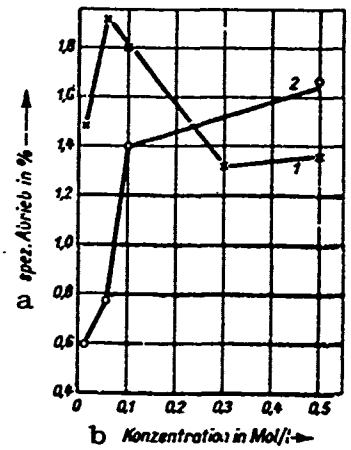

Fig. 8. Influence of Concentration of the Disulfide on the Specific Wear (500 h duration of working); 1st System: Copper/p,p'-Dimethyl Diphenyldisulfide/1,2-Dichloroethane/Air. 2nd System: Iron/p,p'-Dimethyldiphenyldisulfide/1,2-Dichlorethane/Air

Key:
a. Specific wear in % b. Concentration in Mol/l

Mechanical working causes lattice disturbances on a metal surface and creates reactive adsorption sites. Molecules of the liquid phase migrate through diffusion to these surface sites "in statu nascendi." The partner which is more boundary area-active will form the adsorbate. Here, one should not forget that the formation of the adsorption layer in general takes place under non-equilibrium conditions with a supply of free energy. The adsorption layer formed is exposed to continuous mechanical working. Depending on the chemical specifics brought along by the reaction partners, two different reaction possibilities result. The adsorption layer can be "pared off" the surface. The fragments formed continue reaction with the liquid phase and the metallic surface reacts anew with the formation of an adsorption layer. This reaction cycle can continue until one reaction partner is used up or a tribochemical equilibrium is established. Besides this corrosive reaction possibility, as another extreme. There is the possibility that the adsorption layer which has been worked reacts in itself and forms an

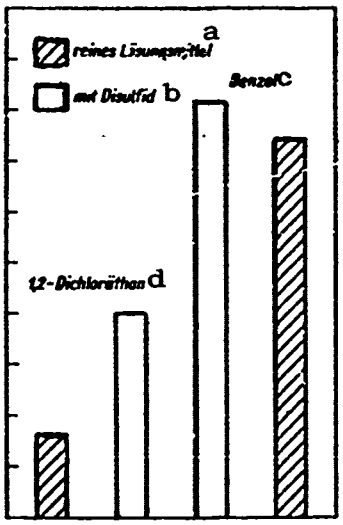

Fig. 9. Effect of Solvent on the Abrasion of Copper; Concentration of p,p'-Dimethyldiphenyl Disulfide 0.1 mol/l, Working 500 h in Air

Key:

a. Pure solvent	c. Benzene
b. With disulfide	d. 1, 2-dichloroethane

energetically more stable reaction layer. This case is observed during surface hardening due to working.

The time between the working phases in a discrete metallic microregion appears to be decisive for the entire course of the reaction. This frequency effect [9], [14], known from literature, can lead to incomplete or no adsorption at all taking place since the adsorption speed is smaller than the working frequency.

In this context it appears important to point out that during friction processes the molecules of the base oil has a 10 times higher probability of hitting an adsorption site than the molecules of the additive. It can be safely assumed that reaction products of the base oil react with the molecules of the additives. This imparts a twofold function to the additives. The reaction, or, more general, the interaction with the metal and the retention of reaction products of the base oil.

The function mentioned last is connected directly with the aging phenomena of a lubricating oil. So far, however, wear and aging have been treated separate from each other.

From the role and importance of tribochemical reactions during friction processes as explained here, it follows that wear and aging must have common causes. In the future both effects will be considered from a uniform standpoint which takes into consideration the importance of tribochemical reactions in the boundary areas.

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