FINSKA KEMISTSAMFUNDETS MEDDELANDEN

SUOMEN KEMISTISEURAN TIEDONANTOJA

REDAKTÖR — TOIMITTAJA

Tor-Magnus Enari

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Utgiven av — Julkaisija
Finska Kemistsamfundet — Suomen Kemistiseura
Postbox 476 Postilokero
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Cationic Surface-Active Amines and their Derivatives — Some Examples of their Use in Technical Processes

Elon Olsson

Liljeholmens Stearinfabriks AB, Stockholm, Sweden.

Of the surface-active compounds, the anionics are well known, whereas the cationics are perhaps less known, at least as far as their industrial use is concerned. As the use of cationic surface-active products is in rapid development, it may be justified in this symposium to mention some of the industrial processes in which these products have got important usage.

The most generally useful cationic surface-active compounds are the straight-chain higher alkylamines and their derivatives that are made from fatty acids. They are produced by allowing the fatty acids to react with ammonia at high temperature in the presence of catalysts, whereby fatty nitriles are formed which are then transformed to primary amines by hydrogenation at high pressures.

$$R\,COOH \xrightarrow{NH_3} RCN \xrightarrow{H_2} RCH_2NH_2$$

By hydrogenation of the nitriles under special conditions, the important secondary amines with two long hydrocarbon chains are obtained.

$$2\ RCN \xrightarrow{H_2} \begin{matrix} RCH_2 \\ \diagdown \\ NH \\ \diagup \\ RCH_2 \end{matrix}$$

Both the primary and the secondary amines may be converted to tertiary amines by methylation, and the tertiary amines, in turn, may be converted into a large number of different quaternary ammonium salts.

$$RNH_2 \xrightarrow{\text{methylation}} RN\begin{matrix}\diagup CH_3 \\ \diagdown CH_3\end{matrix} \xrightarrow{R_1X} \left[\begin{matrix} CH_3 \\ | \\ R-N-R_1 \\ | \\ CH_3 \end{matrix}\right]^+ X^-$$

All amines form salts with both inorganic and organic acids. By combining primary amines with derivatives of acrylic acid, the interesting alkylaminopropionic acids are obtained. These are amphoteric surface-active compounds as they are cationic in acid and anionic in alkaline solutions.

$$RNH_2 \xrightarrow{CH_2 = CHCOOR} RNHCH_2CH_2COOH$$

Thus we have here a family of chemicals which, owing to its unusual richness of variation, displays a very wide range of properties. Common to them all is, however, that they are cationic, i.e., on dissociation the ion containing the hydrocarbon chain becomes positively charged.

$$R\ NH_2 + H^+ \rightleftharpoons R\ NH_3^+$$

As, in practice, most surfaces are negatively charged, it is easy to understand that these cationic surface-active compounds can be very useful for modifying the properties of the surfaces of different products in a desired direction and in this way also effect the properties and behaviour of the product itself.

Adhesion Promoting Agents

One of the most important fields of use of fatty amines is road building. For a good road, it is essential that the adhesion between the stone material and the bituminous binder is both strong and durable. The latter requirement is often overlooked in the ordinary course of testing, but it is, of course, as essential as the former. Silicates are the most often used and also the best materials for road building. They are strongly hydrophilic,

whereas the bituminous binders are strongly hydrophobic. The possibility of getting good adhesion in the presence of water without using special auxiliary agents is therefore very poor. It is in this particular application that amines have recently become of great importance, mainly through the pioneering work of Professor Hallberg and Doctor Arnfelt at the State Road Institute in Stockholm (1), and as a result amines are now used on a very large scale for surface dressing, grouting and making oiled gravel. It is justified to say that it would not have been possible to make an oiled gravel coating if strong and durable, so-called active adhesion-promoting agents had not been available. How then do the amines react with the stone surface? When the binder comes in contact with the wet stone surface, the amine, which has been mixed into the bituminous binder in a proportion of about 1—2 %, dissolves in the water and binds hydrogen to form charged positively ions. These diffuse through the water layer and are adsorbed on the negatively charged stone surface. The big cations are bound relatively firmly and cover the stone surfaces with a hydrophobic layer. The contact angle between stone and water is increased and that between stone and binder is decreased, which leads to a preferential wetting of the stone surface and a displacement of the water. Adhesion is thus obtained, at least temporarily. But it is just as important to get a durable adhesion. The adsorption of the amine on the stone surfaces is, however, reversible, and therefore a rather difficult compromise must be made when choosing the best product. The first requirement is that the adhesion-promoting agent should be soluble in the binder — certain amine salts, e.g., the hydrochlorides, are only very slightly soluble — and at the same time so soluble in water that the concentration necessary for the establishment of a good adhesion can be obtained. Thus the relation between the solubility in water and in the binder must be carefully considered. Neither is too high a solubility in water an advantage as the coating will then be more sensitive to water and thus have a shorter life. This particular problem can be studied in the laboratory, but only by dynamic methods; static methods are not applicable in this case. Using such methods in our laboratory we have found great differences between the long-chain fatty amines and the more hydrophilic polyamines and also that fatty amines of low molecular weight are more sensitive to water. Similar results have been obtained in investigations of flotation, notably those of Götte and Schultz (2), who found that the contact angle on quartz which has been rendered hydrophobic with an amine hydrochloride decreases on washing with water and the more the lower the molecular weight of the amine and the higher its solubility in water (Table 1).

Table 1. Contact angles on quartz. Retention time of air bubbles: 15 minutes; pH = 6.

Collector	n-propylammonium-chloride		n-hexylammonium-chloride		n-dodecylammonium-chloride		n-hexadecylammo-niumchloride		n-octadecylammonium-chloride	
Concen-tration gram per litre	ϑ after		ϑ after		ϑ after		ϑ after		ϑ after	
	Adding of collector	rinsing	Adding of collector	rinsing	Adding of collector	rinsing	Adding of collector	rinsing	Adding of collector	rinsing
0,01	0°	0°	~ 0°	0°	33,5°	<10°	43,9°	28,9°	65,8°	57,5°
0,02	0°	0°	< 10°	0°	41,4°	~ 16°	65,0°	37,7°	75,9°	59,1°
0,05	0°	0°	22,2°	<10°	50,6°	30,4°	69,0°	41,8°	72,6°	63,0°
0,1	0°	0°	18,6°	<10°	53,4°	32,8°	66,6°	56,9°	60,3°	68,4°
0,2	0°	0°	19,6°	<10°	52,5°	30,0°	59,3°	64,6°	32,4°	64,3°

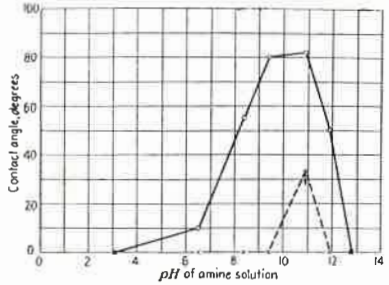

Fig. 1. Contact angles on quartz
o = Angle in solution of 2.5 mg. per litre LAmHCl (pH adjuste with HCl or NaOH).
x = Angle in 10^{-6} N NaOH (free of amine after 10 min. conditioning in amine solution at indicated pH).

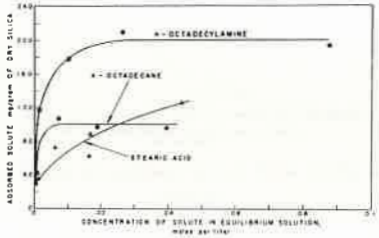

Fig. 2. Adsorption on dry silica surface.

The adsorption of the amines on the aggregate and its contact angles against water and binder is also dependent on the pH. Too high a hydrogen ion concentration can prevent adhesion and can destroy any adhesion already obtained (Fig. 1).

Also too high a concentration of an inorganic base can weaken the adhesion as also high concentrations of certain salts, e.g. $CaCl_2$. Badly eroded felspar can have relatively high concentrations of alkaline products on its surfaces which can interfere with the adsorption of the adhesion-promoting agent.

Different opinions have been expressed and perhaps still prevail on how much of the adhesion-promoting agent must be added to the binder to obtain a satisfactory adhesion. There exists perhaps a tendency to use or to prescribe the use of too small amounts of the adhesion-promoting agents. It is evident that the amount required depends upon many factors, such as the type of adhesion promoting agent, the composition of the stone material, the water content of the chippings, the prevailing conditions at the site of use, and so on. Interesting results which may offer a guide in this respect have been obtained by C. S. Brooks (4) who investigated the adsorption of water and certain aliphatic compounds on the surface of silica. As seen

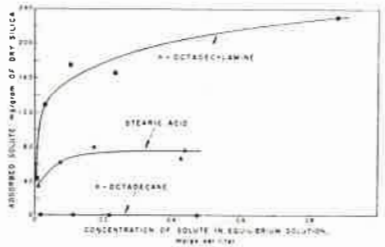

Fig. 3. Adsorption on silica with water monolayer.

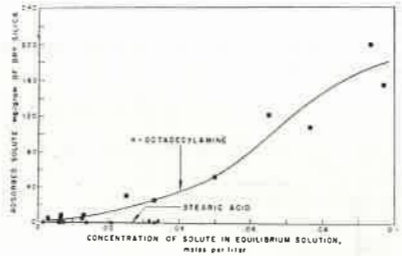

Fig. 4. Adsorption on silica with water multilayer (equivalent to 54 molecular layers).

in Fig. 2, all the tested substances are adsorbed without difficulty when the surface is free of water.

However, when the silica has become coated with a monomolecular layer of water, the hydrocarbon octadecane is no longer adsorbed, but stearic acid and stearylamine are still adsorbed without difficulty (Fig. 3).

When the adsorbed water layer is 54 molecules thick, only the stearylamine is adsorbed (Fig. 4).

The adsorption is, however, slower, which should be remembered in practical work. Perhaps even more interesting are the results obtained by Brooks (4) when he determined the adsorption of water on the surface of silica which had been pretreated in the dry condition with each of the three test substances. As seen in Fig. 5, the hydrocarbon does not prevent the adsorption of water. Stearic acid is a little better at a low relative humidity, but not at a high relative humidity. A siliceous stone surface coated with adsorbed fatty acid cannot withstand the effect of water in the long run and the adhesion will be lost. However, if we look at octadecylamine, the result is quite different. Even at a relative humidity of 100 %, water is not able to displace the amine nor is it adsorbed in quantities large enough to weaken the adhesion. These results have been fully corroborated by practical experience on roads.

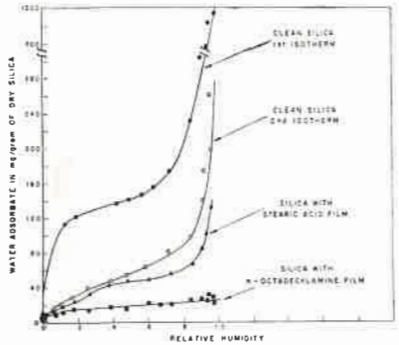

Fig. 5. Water isotherms at 30°C on silica with preadsorbed organic films.

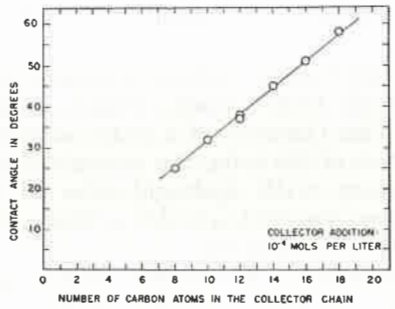

Fig. 6. Effect of the number of carbon atoms in the collector chain on the magnitude of the contact angle on sylvite.

Flotation

Another fieled in which the use of cationic surface-active amines is large and increasing is mineral flotation. Here the problems are closely related to those of adhesion. The technique involves the treatment of mineral particles with suitable substances which, when adsorbed, endow the mineral with hydrophobic properties strong enough to enable flotation to take place. Some of the most important applications of cationic surface-active agents in this field include the flotation of quartz from phosphates, quartz and silicates from iron ore, quartz from felspar, and potassium chloride from sodium chloride. When the flotation of quartz is involved the contact angle depends, as previously mentioned, on the pH of the solution. This also applies to certain other minerals. It is, of course, also dependent on the concentration of amine salt in the solution. If a flotation with a high degree of selectivity is involved, e.g. the cationic flotation of iron ore or separation of different silicates from each other, it is difficult to adjust the conditions so that both a high yield and a high purity are obtained. If, however, the right quantity of amine is used and the work is confined to the right pH range,

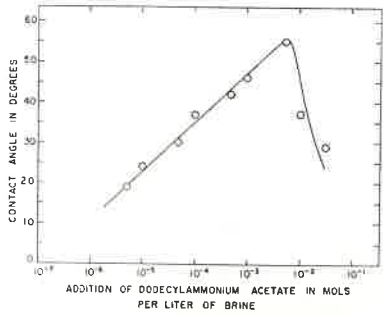

Fig. 7. Contact angle on sylvite as a function of the addition of dodecylammonium acetate in moles per litre of brine. (24 ± 2°C.)

which is usually narrow, it is possible to solve the problem in most cases.

A very interesting type of cationic flotation is the separation of potassium chloride from sodium chloride, a process used on a very large scale. This flotation of a water-soluble salt is done in a saturated solution of the salts, the crystals of which are conditioned by treatment with hydrochlorides of high-molecular-weight fatty amines, mainly C_{16} and C_{18}. Those of low molecular-weight are less effective (Fig. 6).

Remarkably enough, the amines are not adsorbed on the NaCl but only on the KCl crystals and thus the latter may be floated from the salt slurry, leaving the NaCl as a residue. Opinions differ on why the amine is adsorbed only on the KCl, but there is strong reason to believe that this depends on the distances between the ions in the respective crystal lattices. The lattice of potassium chloride has room for the large alkylammonium ion, whereas the lattice of the sodium chloride has not. It has also been surmised that the difference in adsorption depends upon the difference in the hydration of the two salts. Sodium chloride is strongly hydrated and thus can be said to have a protective barrier of water molecules on its surface which is lacking on the surface of the potassium chloride crystals. In this flotation, however, care must be taken not to add too much amine as the angle of contact decreases by overdosage (5). This is perhaps due to the formation of a second layer of ions that are oriented in the opposite direction (Fig. 7).

Pigment Manufacturing

Most pigments are manufactured in a water phase and are usually hydrophilic. On drying, the particles, which are initially very small, are agglomerated to larger aggregates which are often also harder. Before these can be used in lacquers, they must be broken down effectively again to give sufficient depth of

colour and lustre. This is usually performed by grinding the pigments dispersed in a vehicle on a roller mill. However, the attainment of the required fine dispersions of certain pigments takes an uneconomically long time on the roller mill and thus the capacity is low and the power consumption high. Pigments especially difficult to disperse are Prussian Blue, Chrome Green, Toluidine Red and some others. If suitable surface-active agents are adsorbed on the pigment grains, the difficulties are to a large extent decreased. They render the pigment hydrophobic and facilitate its wetting with oil and the treated particles have a lesser tendency to agglomerate again to larger aggregates. In this way it is often possible to obtain degrees of dispersion which would be impossible to attain otherwise and the saving in power and time can be considerable, in some cases as much as 50 %. The dispersing agents most commonly used are mainly of the cationic type, e.g., the oleates of alkylpropylene diamines, quaternary ammonium compounds, containing two long alkyl chains, and certain tertiary amines. Different pigments require different surface-active amines or combinations of them and the quantity depends, of course, on the difficulty of dispersion and the desired grain size of the pigment. The requirements as to the properties of the pigments have lately been increased more and more and the development now moves along the lines of actually treating the pigment with surface-active material at the time of manufacture, so that the pigments are sold already conditioned. They have thus been rendered hydrophobic and can be easily dispersed in oils. One example is Prussian Blue which on treatment with the amphoteric laurylaminopropionic acid becomes soft, fine-grained and easily dispersible, even after drying. It is also possible to treat other pigments and also extenders for rubber and plastics in such a way that both these and the products produced from them get greatly improved properties. Another method often used to preserve the initially high dispersion of the pigment is "flushing". This method makes it possible to transfer the pigment into oil directly from its aqueous suspension or the filter cake in which it has been obtained from its manufacture. In this way drying is unnecessary with its disadvantages of high cost and risk of agglomeration. The flushing is carried out in special machines in which the aqueous pigment-suspension is kneaded with oil to which surface-active agents have been added to render the pigment hydrophobic. The oil thus displaces the water from the pigment and this water may then, after further treatment, be squeezed out of the pigment paste and drained off. The final traces of water may be removed by drying in special vacuum dryers. The pigment paste thus obtained can be used directly as a component in different types of lacquer systems.

Anti-caking Agents

In recent years, the problems posed by "caking", that is, the agglomeration of certain hygroscopic salts, have forced themselves upon the attention of manufacturers as the occurrence of caking in practice produces quite noticeable difficulties in handling with attendant increases in costs. Increasing numbers of consumers demand non-caking, free-flowing chemicals. The chemicals concerned are usually NH_4NO_3, NH_4Cl, $(NH_4)_2SO_4$, KCl, urea, and a great number of mixtures used as fertilizers, e.g., superphosphate. The caking is mainly caused by variations in temperature and humidity which cause repeated recrystallisation and dissolution in the layers of saturated salt solution which always exist on the crystal surface. The result is that the crystals grow together by forming bridges of new crystals and form hard lumps or in big piles complete mountains of hard salt which must be blasted with dynamite before it is possible to put the material into sacks. This is yet another area where surface-active materials have turned out to be helpful. It is evident that for the additive to be of any use it must either possess almost the same lattice constants as the salt which it is required to modify or be able to react chemically with it. Octadecylamine is an effective anti-caking agent for both NH_4NO_3 and KCl. The amine reacts chemically with NH_4NO_3, after it has been spread on the surface and subsequently adsorbed to form free ammonia and octadecylamine nitrate on the surface of the crystal. This nitrate is insoluble in water and strongly hydrophobic. In the case of KCl the octadecylamine ions are also adsorbed on the surface of the crystal, but instead of reacting they penetrate into the crystal lattice and cause the surface of the crystal to become hydrophobic, which in turn decreases the tendency to cake. An interesting fact which has not been investigated to any extent is that the saturated primary amines and their acetates are best for KCl, while the corresponding hydrochlorides or certain long-chain tertiary amines are better for potash superphosphate. Octadecylamine is ineffective for urea while octadecylurea gives very good results. The closely related materials octadecylguanidine acetate and octadecylbiguanide, are, strange enough, ineffective.

Softeners and Antistatic Agents

Most textile fibres are negatively charged and therefore easily adsorbe cationic surface-active agents. Hydrogen bonds are formed which are relatively strong. Two different effects are observed depending on the agent used. Quaternary ammonium compounds containing one long hydrocarbon chain produce an antistatic effect, that is, the fibres lose their tendency to build up a static charge of electricity by friction. There are certain

synthetic fibres, especially nylon and terylene, in which this static electricity is very irritating, and a treatment for decreasing the charge is therefore desirable. If, however, fibres are treated with quaternary ammonium compounds which contain two long hydrocarbon chains, a different effect is observed in that the fibres become softer and the fabric gets a better handle. Such agents have been used for some time in the USA in the household as additives to the last rinsing water in washing mashines and it seems that they will soon spread also to Europe. Products containing them have in fact already been put on the market in England, Germany and Denmark.

Corrosion Inhibition

Cationic surface-active materials are also adsorbed on the surface of metals. This adsorption renders the metallic surface hydrophobic and thus it is possible to obtain two effects, an inhibition of corrosion and a better heat-transfer through dropwise condensation. Certain fatty amines therefore are of great importance in industries where these effects may be utilized. They are mostly used for this purpose in the pulp and paper industries but of course they can be used in all industries where corrosion and heat-transfer are economically important factors. In the paper industry the use of stearylamine has led to an increase of between 5 and 7 % in the capacity of the machines and this is no small improvement. Not only this, but at the same time a suppression of corrosion has been noticed and the heat-transfer surfaces have remained clean and effective. It is also interesting to note that the stearylamine can be used as an effective, but yet mild detergent in plants with hard deposits of rust and other corrosion products in the tubes and on heat-transfer surfaces. Addition of stearylamine for a time to the steam can effectively clean whole plants and improve their efficiency.

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The Breaking of Asphalt Emulsions

Axel O. Bohn.

Laboratoriet for vej- og jernbanebygning samt byplanlaegning, Danmarks Tekniske Hojskole, Kobenhavn.

Introduction

The asphalt bitumen obtained as a pitch-like residue when asphalt-base petroleums are distilled, has attained great importance as a binder in road construction. The high viscosity of asphalt bitumen gives the pavement the ability to resist the erosion of traffic, but makes it necessary, on the other hand, to facilitate the contact between the binder and the aggregate. Here profitable use has been made of emulsions of asphalt bitumen in soap solutions.

If such an emulsion is brought into contact with an aggregate, some of the emulsion will in many cases coagulate, even without a simultaneous evaporation of water from the emulsion. This tendency of the emulsion to break in contact with an aggregate can be estimated by means of the Weber and Bechler method (1), where the weight of the bitumen which has coagulated after a certain time on the stones in such a form that it cannot be removed by rinsing with distilled water is determined. Weber and Bechler, as well as Keppeler, Blankenstein, and Borchers (2), found that the emulsions became more stable on adding potassium or sodium hydroxide. Furthermore, it was ascertained that highly active stones lost their ability to break the emulsions when treated with alkalis. The acidity of the stones as determined with alkali showed a clear positive correlation with the breaking ability. Finally it was observed that a soap solution in contact with an active aggregate such as basalt became turbid which turbidity was assumed to be due to fatty acid. On the basis of these observations, the conclusion was drawn that the acidity of the stones caused the emulsions to break (the acid action theory).

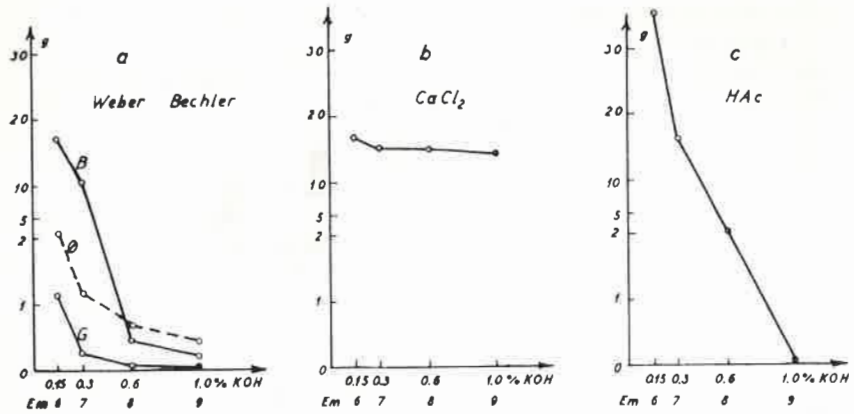

Figure 1. Coagulated asphalt in a series of emulsions with increasing alkalinity.
1a. In the presence of aggregates G (granite), B, (basalt) and Ø (Oeland limestone).
1b. In the presence of $CaCl_2$.
1c. In the presence of acetic acid.

Weber and Bechler experiments

Figure 1 a shows how the Weber and Bechler number — which is the amount of bitumen coagulated on 100 g of 0,5—1 mm crushed stone particles which have been in contact with 500 g of emulsion for one hour — decreases with increasing KOH content in a series of emulsions (nos. 6—9). The emulsions all contained 50 % asphalt bitumen and 0.6 % oleic acid (HOl). The aggregates were a strongly active basalt, a weakly active granite, and a limestone from Oeland. It is seen that the breaking numbers for the last-mentioned rock decrease relatively little with increasing alkalinity.

Often the electrolyte stability of emulsions is estimated. Figures 1 b and 1 c show how much bitumen is coagulated from 500 g of emulsion on adding 2.2 ml of 0.1 N $CaCl_2$ or 3.6 cm^3 of 0.1 N acetic acid. The stability of the emulsions towards $CaCl_2$ is almost independent of the potassium hydroxide content, whereas the stability towards acetic acid, like the Weber and Bechler number, decreases with increasing alkalinity of the emulsion.

This is in agreement with the acid action theory, but it is improbable that the stone acids must be supposed to be as strong as acetic acid. The coagulation numbers for boric acid are thus $\simeq 0$. If the same experiments are made with a series of emulsions with a higher content of oleic acid, the Weber and Bechler numbers and the stability towards acetic acid is diminished little, whereas the stability towards calcium chloride is strongly diminished.

The content of exchangeable ions in the aggregates

Aqueous stone extracts have only a weak coagulating action. But extraction with solutions of electrolytes such as KOl, NH_4Ac or KCl removes considerable amounts of calcium (and Mg). A 0.1 N solution of NH_4Ac, an ion exchange reagent often used by agricultural chemists, dissolves 2.2 milliequiv. of Ca and Mg from 100 g of crushed basalt stone in the course of an hour. This was the amount of stone used in the above-mentioned determination of the stability toward calcium chloride. Only 1.5 meq of Ca and Mg are dissolved in 0.05 N NH_4Ac, and peculiarly enough, even a little less, 1.05 meq of Ca and Mg is dissolved in 0.05 N KOl. in spite of the low solubility of $CaOl_2$ An examination of the sediment formed by the reaction between KOl and basalt gave the result that it did not, as assumed earlier, consist of fatty acid, but of $CaOl_2$; this is a decisive proof against the acid action theory.

It still remained to determine why the Weber and Bechler numbers decrease strongly with increasing alkalinity. The curve for the $CaCl_2$ stability did not show a decrease. An explanation was found in the pH dependence of the calcium exchange. When the exchange with a KCl solution was measured by varying the pH by small additions of pH-regulating compounds (HAc, NH_4Ac, KOH or mixtures of them), it was found that calcium was bound somewhat more strongly to basalt and other aggregates at high pH values.

Experiments using aggregates with exchanged ions

Basalt is an ion exchanger whose most common ion constituent in the natural state is calcium; this cation can be replaced by treating the stone with different electrolytes. On repeating Weber and Bechler's experiment after treating the basalt with sodium hydroxide, the Weber and Bechler number decreases, as expected, to a quite small value; for emulsion 6 the decrease is from 19.1 to 0.82. At the same time the acidity falls from 3.6 meq/100 g (this means that 100 g of basalt will bind 3.6 meq of OH ions after treatment for one hour with 0.5 N KOH) to 0.62, and the content of exchangeable calcium ions (measured after one hour's contact with 0.1 N NH_4Ac) from 2.2 to 0.5. It is interesting to note that if basalt is treated with sodium chloride solutions, the Weber and Bechler number decreases to a still lower value, 0.19, and the content of exchangeable calcium ions decreases to the very low value 0.064. Some of the hydrogen ions of the basalt are also exchanged, but the acidity remains at the rather high value 1.42 meq/100 g (compared with 2.2 for untreated basalt). It is hence possible — quite contrary to the acid action theory — to have very low Weber and Bechler numbers for aggregates with a considerable acidity.

The experiment was confirmed by experiments using an inorganic water-softening ion exchanger (zeolite), the ion exchange capacity of which was far greater than that of the natural aggregates.

Blocking-up of the stone surface

In many cases the observed Weber and Bechler numbers are smaller than those expected from the content of exchangeable calcium ions owing to the stone surfaces being blocked by a coagulated layer of bitumen so that no more calcium ions pass into the emulsion. In one experiment, a Weber and Bechler number of 19.1 was measured for basalt. After the experiment, the crushed stone was washed free from bitumen with benzene; a Weber and Bechler number of 10.4 was then measured for this crushed stone. A 3rd and a 4th Weber and Bechler experiment on the same material after washing with benzene between experiments gave the numbers 4.9 and 1.8 respectively. After the last experiment, the content of exchangeable calcium ions was only 0.24 meq/100 g against 2.6 for the untreated basalt. The acidity was now 1.2 meq/100 g compared with the original 3.2. For limestone, however, the breaking activity remained almost unaltered in repeated Weber and Bechler experiments. Whereas basalt continues to break the emulsion in these experiments until the content of exchangeable calcium ions has been used up, the breaking ability of the limestone does not change because the reaction between soap solution and aggregate has not the character of an ion exchange reaction.

Adhesion between the stone and binder in the presence of electrolytes

The blocking-up experiments show that there is no simple connection between the ion exchange properties and the breaking ability. The blocking-up phenomenon is connected with the adhesion problem often discussed in the asphalt literature. Riedel and Weber (3) have devised an adhesion test that measures the adhesion between a bituminous binder and an aggregate in the presence of a water phase; the adhesion is found to decrease with increasing alkalinity of the water phase.

This is surely the most important reason for the decrease of the breaking number in strongly alkaline emulsions. In emulsions rich in alkali, the bitumen particles are kept away from the stone surfaces. The calcium ions set free by ion exchange must therefore preferentially form insoluble lime soap with the fatty acid ions which are not adsorbed to the bitumen drops, but which are distributed as molecules or in the form of micelles in the dispersion medium. The smaller breaking in the alkaline region is supported by the decreased calcium exchange with increasing pH.

In emulsions of lower alkalinity the repulsion between bitumen drops and the stone surface will be smaller so that the calcium ions set free by ion exchange will, to a wide extent, be able to precipitate calcium soap of the fatty acid anions adsorbed to the bitumen drops. This can, however, be counteracted in some degree by augmenting the amount of fatty acid in the emulsion; a series of emulsions rich in fatty acid are more stable than a series poor in fatty acid.

The earlier found correspondence between breaking action and acidity is due to the fact that stone aggregates with a higher acidity normally also contain many exchangeable calcium ions.

The adhesive ability of basalt, granite and Oeland limestone has been examined with the Bartell-Halberg displacement cell (4). Here the adhesion tension is calculated from a measurement of water pressure, the pressure necessary for displacing bitumen sucked up in a column of compressed stone powder. It is the product of the interfacial tension of water — binder and the cosine of the contact angle. The experiments were made with untreated aggregates and with aggregates which had been treated with sodium chloride or hydroxide.

The adhesion tension is seen in the table below:

	A, dyne/cm
Basalt, untreated	11.7
» treated with NaCl	1.6
» » » NaOH	0.6
Granite, untreated	8.9
» treated with NaCl	0.9
» » » NaOH	0.6
Oeland limestone, untreated	13.0
» » treated with NaCl	13.0
» » » » NaOH	10.6

The adhesion tension is seen to be reduced by exchange with sodium ions. Treatment with sodium chloride is not as effective as treatment with sodium hydroxide. A treatment of limestone, which has no ion exchange qualities, with sodium chloride or hydroxide has only a slight influence, however, in agreement with the observation that Oeland limestone is an aggregate with the greatest blocking-up tendency against alkaline emulsions and for which the breaking numbers against emulsions were reduced least with increasing excess of hydroxide.

Summarizing, the conclusion must be that the breaking in a Weber and Bechler experiment is principally due to the emulsifier being destroyed by the formation of insoluble calcium (and Mg) soaps. The examined anion emulsions will transform the aggregates according to their greater or smaller ion exchange ability

into aggregates with more or less diminished adhesive properties. At the same time calcium ions are displaced in an amount dependent on the pH of the emulsion as well as on the ion exchange capacity, the content of calcium carbonate, and on the degree of the blocking-up of the stone surface by precipitated bitumen. These calcium ions will precipitate calcium soap both from the alkali metal soap which is present as an emulsifier film around the emulsion particles, and from the alkali metal soap which is found — principally in the form of micelles — in the continuous phase. The coagulation which is measured will therefore depend on how these calcium ions distribute themselves among the fatty acid anions in the emulsifier film and in the micelles, as well as on the amount of fatty acid anions and the amount of coagulating calcium ions which become available.

This distribution is again dependent on the attraction between stone and asphalt bitumen which manifests itself in the measured adhesion ability, which decreases with increasing potassium hydroxide content in the water phase.

The acidity of the stones, or the adsorption of the emulsifier (5) which was supposed earlier to be the most important cause of the breaking of asphalt bitumen emulsions, seems to be of lesser importance.

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The Effect of Surface-Active Substances on Clay Suspensions and Cement Slurries

Per Ekwall

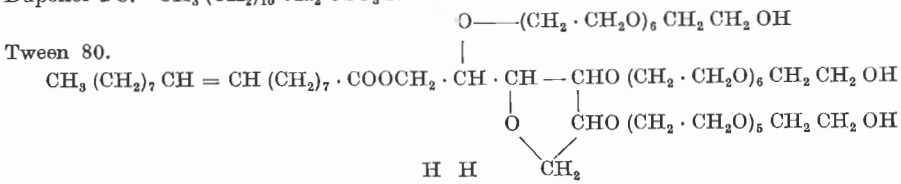
Institute of Physical Chemistry, Åbo Akademi, Åbo, Finland.

The results that I intend to describe briefly may illustrate some fundamental processes in the interaction of surface-active substances and suspensions of minerals. The experiments were carried out a few years ago on industrial raw materials in collaboration with the Pargas Kalkberg A/B, Willmanstrand.

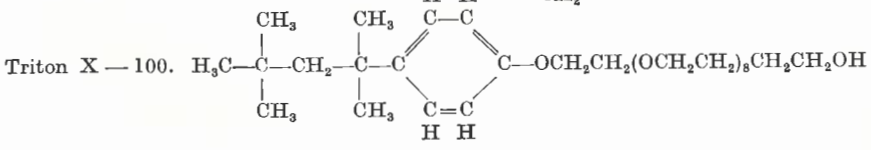
Surface-active substances greatly alter the viscosities of clay suspensions. The agents whose action we studied were Duponol PC, Tween 80 and Triton X-100. The viscosities of the suspensions were measured with a rotational viscometer (Epprecht TV) which only gives apparent viscosities. The clay was from Willmanstrand; its surface area as determined in the laboratory in Willmanstrand by the method of Lea and Nurse was 27850 sq. cm per gram

Duponol PC. $CH_3(CH_2)_{10}CH_2OSO_3Na$

Tween 80.



Triton X — 100.



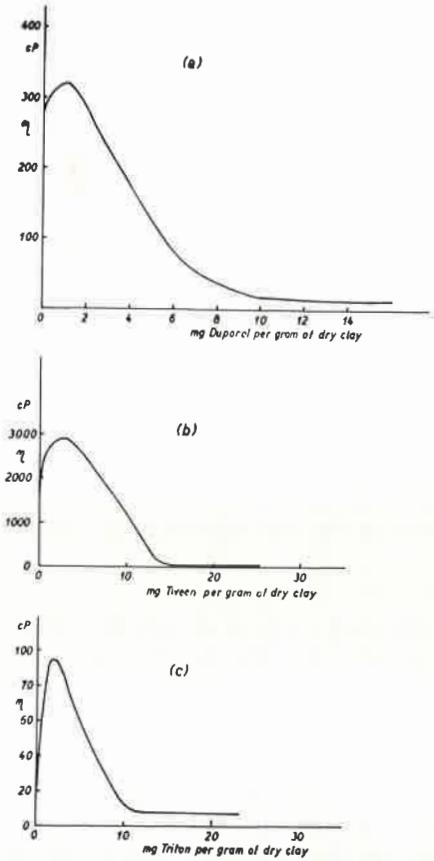


Fig. 1. The effect of surface-active substances on the viscosity of clay suspensions.
a) The effect of Duponol PC on the viscosity of a clay suspension containing 51 per cent water.
b) The effect of Tween 80 on the viscosity of a clay suspension containing 43,3 per cent water.
c) The effect of Triton X-100 on the viscosity of a clay suspension containing 60 per cent water.

The effect of the surface-active substances on the viscosity is shown in Fig. 1. The variation of the viscosity is very similar irrespective of the clay content of the suspension: small amounts of the surface-active substance effect a pronounced increase in viscosity, but with greater amounts the viscosity in all cases decreases to a very low value that does not change further when more of the surfactant is added. The changes in viscosity produced by the different surface-active substances are similar.

In order to find the reasons for these viscosity changes, we studied the ability of the clay particles to adsorb the surfactants.

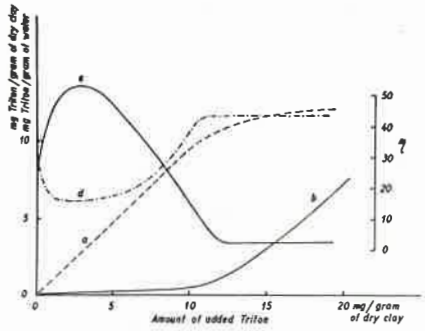


Fig. 2. The effect of Triton X-100 on a clay suspension containing 52,5 per cent water. The abscissa gives the total amount of added surface active substance in milligram per gram of dry clay.

a) The adsorption of Triton in milligram per gram of dry clay.
b) Equilibrium concentration of Triton in the aqueous phase of the suspension in milligram per gram of water.
c) The viscosity of the suspension.
d) The water content of the clay sediment after centrifugation in per cent.

The amounts adsorbed vary as shown by curve a in Fig. 2. Up to a certain concentration the agent is strongly adsorbed, but above this concentration the amount adsorbed increases very slowly or is negligible. This is shown by the curve b which plots the equilibrium concentration of surface-active substance in the aqueous phase of the suspension. Curve c reveals that the maximum decrease in viscosity coincides with the concentration where no further adsorption takes place. Curve d plots the water bound by the clay particles. The water content decreases at first, passes through a shallow minimum, and increases to a level where it remains practically unaltered as soon as the adsorption stops.

Our study shows further that all the values of the adsorbed amounts for a surfactant lie on a single adsorption isotherm irrespective of the clay content of the suspens on. The isotherm shows a sharp break point which indicates the end of the adsorption. The adsorption isotherm for Triton X-100 is shown in Fig. 3. The break point is located at an equilibrium concentration of 0.0007 mole per litre, which is above the CMC, 0.0002 mole per litre, of the surface-active substance.

The amounts of surface-active substances adsorbed by the clay at the viscosity maximum and at the viscosity minimum where no further adsorption occurs are given in Table 1. The areas available to each surface-active molecule on the surface of the particle are also shown in the table. When the maximum amount is adsorbed, the area per molecule is close to that which

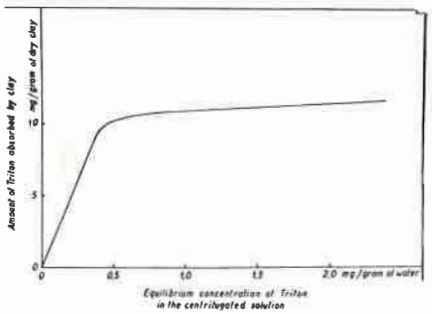


Fig. 3. The adsorption of Triton X-100 on clay in suspensions containing from 46 to 78 per cent water. The abscissa gives the equilibrium concentrations of Triton in the aqueous phases of the suspensions in milligram per gram of water. On the ordinate the adsorbed amounts of Triton in milligram per gram of dry clay.

Table 1. The connection between the adsorption of a surface-active substance on clay and the influence on viscosity.

Surfactant	Adsorbed amount of surfactant		Area per molecule of adsorbed substance	
	mg per gram of dry clay		Å² per molecule	
	At viscosity maximum	At maximal decrease of viscosity	At viscosity maximum	At maximal decrease of viscosity
Duponol PC		~ 4		28.0
Tween 80	~2.4	15	259	43.0
Triton X-100	~1.8	11	168	27.6

the molecules would occupy in a densely packed monolayer. It would, however, be more natural to assume, in the classical manner, that the agent is adsorbed as a less densely packed double layer with the hydrophilic groups of the molecules in the inner layer against the clay surface and those of the molecules in the outer layer against the water. These structures would be in accord with the observed secondary phenomena. The area per molecule is actually very large at the viscosity maximum, but still of a magnitude that implies that the particle surface could be covered by hydrocarbon chains in a monolayer. The formation of such a monolayer would be expected to effect an increase in viscosity at the same time as the hydrogen bonds by which the solvated water is bound to the surface of the particles are broken down and the water content of the clay decreases. When

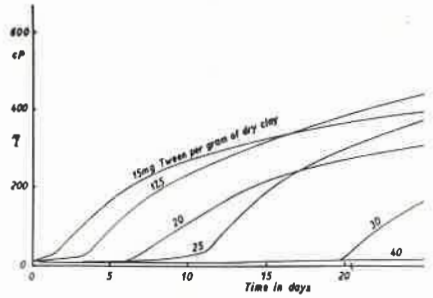


Fig. 4. The variation of the viscosity of clay suspensions containing various amounts of Tween 80. as a function of time. The water content of the clay suspension 55 per cent.

the outer layer of molecules with the hydrophilic groups and their hydration water pointing outwards is formed the total amount of water bound to the clay particles increases again at the same time as the viscosity decreases.

These first stages of the adsorption and the associated secondary processes take place very rapidly. But by and by another adsorption phenomenon appears (Fig. 4). The content of free surface-active substance in the aqueous phase is observed to decrease gradually. When the equilibrium concentration falls below the value required for complete adsorption and a maximal decrease in viscosity, the viscosity begins to increase slowly. These changes may be ascribed to a diffusion into the particles, whereupon the inner surfaces become covered. More surface-active agent is thereby taken up and the coverage of the outer surfaces becomes less complete.

In contrast to the case with clay suspensions, we have observed no effect of nonionic surface-active substances on the viscosities of limestone suspensions (limestone from Willmanstrand; surface area 3070 sq. cm per gram). The changes in viscosity

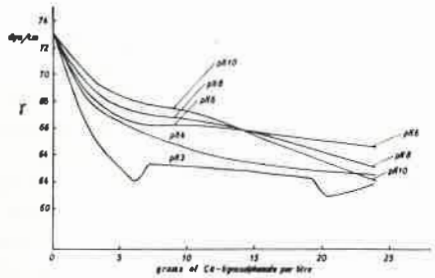


Fig. 5. The surface tensions of aqueous solutions of calcium lignosulphonate at different pH. 20°C.

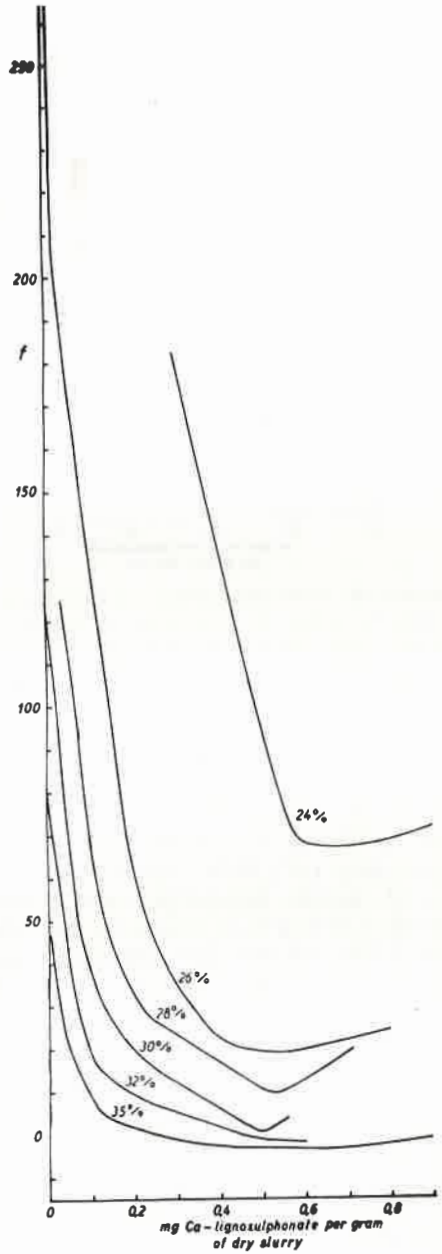


Fig. 6. The yield value of the raw slurry as a function of adsorbed amount of calcium lignosulphonate.

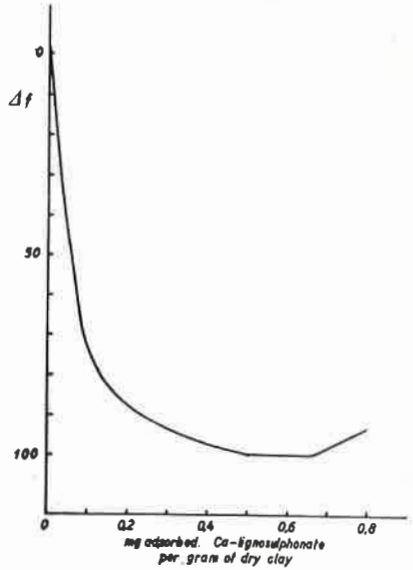


Fig. 7. The decrease in the yield value of the raw slurry in per cent of the total decrease which may be achieved by addition of calcium lignosulphonate as a function of adsorbed amount of calcium lignosulphonate.

noted with mixtures of clay and limestone are approximately proportional to their clay content. This was found to be true also for cement slurries (slurry from Willmanstrand containing clay and limestone in the ratio 5:95; the surface area 3440 sq. cm per gram). The addition of nonionic surface-active substances effected in these cases very little change in viscosity.

The addition of calcium lignosulphonate to slurries, however, gave rise to marked changes in viscosity. The above-mentioned slurries were used. The calcium lignosulphonate was isolated from spent sulphite liquor. (Tappi 629 m — 53) and contained 5.3 per cent calcium. The surface tensions of aqueous solutions of this calcium lignosulphonate are plotted in Fig. 5; the surface tensions were measured with a Du Noüy tensiometer.

A similar study as above was carried out to determine the adsorption of lignosulphonate by the slurry and the influence of this adsorption on the viscosity of the slurry. At this time a rotational viscometer (Epprecht STV) was at our disposal which made possible the measurement of the yield value and the plastic viscosity. Fig. 6 shows the relationship between the yield value and the amount of adsorbed lignosulphonate in milligrams per gram of dry matter in the slurry. The yield value is seen to decrease rapidly. It is possible to draw a common curve for all slurries

Table 2. The connection between the adsorption of calcium lignosulphonate on raw slurry and the influence on viscosity.

Adsorbed amount of lignosulphonate		Area per equivalent of adsorbed substance	
mg per gram of dried slurry		Å² per gram equivalent	
At 75 per cent of total effect of viscosity	At maximal effect of viscosity	At 75 per cent of total effect of viscosity	At maximal effect of viscosity
0.1	0.5	about 500	about 100
mg per sq. cm particle of surface			
$2.5 \cdot 10^{-5}$	$12.6 \cdot 10^{-5}$		

containing from 26 to 35 per cent water by plotting as the ordinate the decrease in the yield value as a percentage of the maximal (Fig. 7). The maximum effect is noted when about 0.5 milligrams of lignosulphonate is adsorbed per gram of dry matter. The area per equivalent in the adsorbed layer is then 100 Å² (Table 2).

Our studies thus show that the adsorption of surface-active agents on mineral particles is a well-defined phenomenon and that this adsorption can be relatively easily measured experimentally. The adsorption and the changes that thereby arise at the surfaces of the particles in turn lead to secondary changes in the properties of the suspension; these changes may be very pronounced in some cases. It is therefore always advantageous in a study of the effect of surface-active agents on mineral suspensions to examine the degree of adsorption. A knowledge of the form of the adsorption isotherm makes it possible to survey the course of the adsorption and to anticipate also the secondary phenomena. The industrial utilisation of flotation processes is based on adsorption studies, but there are many other technical processes (e.g. in the cement and ceramic industries, in the manufacture of paints, in soil stabilisation and roadbuilding etc.) where the necessity and advantage of knowing the adsorption phenomena, the fundamental process, have not been recognized to a sufficient extent.

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Tensides in the Production of Pulp and Viscose Rayon

Fred Gärtner

Berol AB, Gothenburg, Sweden.

When the technical use of tensides (surface-active agents) is discussed, it is almost always a question of the addition of synthetic tensides to different systems. However, we can hardly discuss the different effects of the synthetic tensides in the pulp and viscose industries without due consideration of the naturally available tensides or, more correctly, consideration of the tensides which are formed in pulp manufacture from the resin and wax always present in all types of wood.

Resin contains saponifiable and unsaponifiable components. A saponification takes place in the alkaline sulphate cook or in the caustic extraction which often follows an acid sulphite cook. Soluble alkali metal soaps of fatty and resin acids are formed. These soaps are surface active in alkaline solutions, but are converted to insoluble acids in acid solutions.

The formed soaps represent only a relatively small part of the pulp weight, but they have the well-known characteristics of tensides: small amounts produce large effects.

If we look at cellulose manufactured for the viscose industry, a high resin level in the pulp might produce the following undesired results:

A) Discoloration of the rayon fibres and cellulose films.
B) Deterioration of the fatigue results of tyre cord.
C) Foaming in the deaeration of viscose.
D) Clogging of the spinnerets.

If we extract too much of the resin from the pulp, the following difficulties may be expected:

a) An alkali cellulose will be formed which is difficult to shred.
b) Poor viscose filtration.
c) Dull viscose fibres (milkiness).

The ideal solution of the problem is to completely remove the naturally occurring resin with its varied composition and to replace it with a suitable amount of a synthetic tenside with desirable and constant properties. However, this solution is too expensive and we have to compromise. This means that nowadays the total resin content of the pulp normally runs at two or three tenths of a percent. The soluble soaps are only a small fraction of this amount. The viscose maker or sometimes the pulp producer adds the synthetic tensides which are considered appropriate in each case.

A large part of the resin is removed by an alkaline treatment of a pulp. The soaps formed facilitate the dissolution and dispersion of the unsaponified components. Very often, however, the soap concentration is insufficient to give a satisfactory result. By increasing the soap concentration it is possible to improve the result and it is also a well-known trick to add tall oil fatty acid in this production step. A further decrease of the resin content can be attained by a stronger alkaline treatment, but then other properties of the pulp may be influenced in an undesirable way. Without changing the conditions of the caustic extraction it has often been possible to decrease the resin level further by adding nonionic tensides. The optimum ethylene oxide chain length and hydrophobic part of the tenside are determined by the temperature during the extraction, but also the alkali concentration and resin type have to be taken into consideration. The effect increases with the amount added but a complete removal of all resin is not normally possible. This situation depends on the varying accessibility of the resin due to the anatomic structure of the wood. The canal cell resin is relatively easy to make hydrophilic and dispersible, but the ray parenchyma resin is considerably more inaccessible.

The presence of soaps is not always advantageous. In the bleaching of the pulp under acid conditions, free fatty and resin acids are precipitated. Precipitation can be caused also by calcium ions in an alkaline step. This occurs, for instance, when calcium hypochlorite is used as bleaching agent. The pitch often forms sticky deposits which lead to considerable problems in pulp production. The free fatty and resin acids and the calcium soaps can be dispersed with different tensides and also in this case the nonionic products have found widespread use. The usual additions are no greater than a few tenths of a percent based on the weight of the cellulose. This addition is of the same order of magnitude as the amount of resin.

The tensides used as additives in viscose in the production of rayon were anionic (sulphonated oils) at first, but they have been replaced to a large extent by nonionics (ethoxylated fatty alcohols, alkylamines and alkyl polyamines). This trend is due

to disadvantages connected with the anionic groups. Considerable problems have arisen from their tendency to foam strongly and to form insoluble heavy metal salts. They are also incompatible with the cationic additives used in the spin bath. Cationic tensides are not used in the viscose because of the negative charges of the resin particles.

What can the synthetic tensides do as viscose additives? An addition of synthetic tensides to the alkali cellulose may facilitate shredding sometimes. This is a question of "lubrication". The result is only noticeable when the pulps have a very low resin content, e.g., prehydrolysed sulphate pulps or special sulphite pulps. In normal sulphite pulps the resin content is obviously high enough to ensure a satisfactory "lubrication". The improvement of the shredding can be measured by determining the liter weight of the alkali cellulose as a function of shredding time.

The tensides influence the evenness of the xanthation and the associated ease of viscose filtration and the number of gel particles in the viscose. Also in this case the synthetic tensides are most effective with low-resin pulps. Anionic, cationic and nonionic tensides will all improve filtration, although they vary somewhat in performance. It might seem unimportant which tenside is chosen for the viscose when the main problem is poor filtration. However, it is not that easy. Whatever is added at an early stage of the process will remain in the viscose through all the following stages and all the consequences of the addition must be clear before choosing the tenside.

The emulsifying power of resin soaps is low and often synthetic tensides have to be added to the viscose to decrease the development of dullness (milkiness) in rayon fibers. Dullness will easily arise when the carbon bisulphide content is high or when the spinning is performed with an unripe viscose. In this case it is necessary for the tenside to have excellent emulsifying properties in an acid environment. Carbon bisulphide is liberated when the viscose is acidified during the spinning. The dullness of the fibers is caused by small carbon bisulphide droplets which have not diffused fast enough and have been caught under the outer coagulated layer of the fiber. Only a few tensides are effective in preventing yarn dullness. They are either ethylene oxide adducts of alkylamines and alkylpolyamines or certain types of sulphonated vegetable oils.

The fine openings in the jets may be plugged by different components in the viscose. As examples, inorganic salts like iron sulphide and calcium carbonate, silicon dioxide (sand) and resin particles, and insoluble metal soaps of fatty and resin acids may be mentioned. In preventing this plugging the nonionic tensides are superior to the anionic ones. They have a very noticeable effect on the spinning life of the jets, which from the quality

and production points of view is of very great importance. The hydrophobic particles are rendered hydrophilic and are prevented from forming deposits on the walls of the jet openings.

Some nonionic tensides are used as modifiers in the production of tyre cord and rayon staple of the super type. The modifiers in combination with the trithiocarbonate of the viscose and the zinc ions of the spin bath influence the coagulation and the regeneration of the fibers and thereby the tensile strength, cross section, dyeability, compactness and fatigue of the latter. Both the dry and wet tensile strengths are improved. The low wet strength is a serious disadvantage of normal rayon fibers, but the modifiers provide a means of overcoming this disadvantage.

Besides the ethylene oxide adducts, also amines and polyethylene glycol act as modifiers. For the modifying properties of the nonionic ethylene oxide adducts, their ability to lower surface tension is probably unimportant.

Tensides are used also as spin bath additives. In this case it is important to find products that make the surfaces of the jets as well as the surfaces of the thread guides, heat exchangers, pipe lines in the spin bath system, and so on, hydrophobic. Sulphur itself and other insoluble sulphur compounds are formed during the spinning and have a strong tendency to form troublesome deposits which hinder smooth production. Only cationic tensides are suitable for the formation of these hydrophobic layers.

Owing to lack of time, it is unfortunately not possible to go into the details of all the problems involved in the use of tensides in the pulp and viscose industries. However, I hope that the important role the tensides play as emulsifiers, wetting and dispersing agents has become clear. Tensides have proved to be very good assistants in our endeavours to improve industrial processes.

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Pitch Control in Paper Mills — A Problem of Surface Chemistry

Swedish Forest Products Research Laboratory and Central Laboratory of the Swedish Fibre Board Mills, Stockholm.

Ernst Back

The Problem

The sapwood and heartwood of all wood contains a minor amount of low molecular weight, oleophilic organic material with low water solubility. This material, commonly called resin, is in the sapwood distributed in resin canals and in the ray parenchyma cells. This resin is retained in the sulphite pulp and groundwood and may then cause problems in paper production, mainly owing to the deposition of resinous matter, the so-called pitch, on parts of the machinery. Several tons of resin pass through a newsprint paper machine producing 200 tons of paper a day. A pitch deposit of only a few hundred grams on the paper machine wire or on other important machinery may give rise to significant production troubles.

The Mechanism of Resin Deposition

A study of the mechanism of resin deposition on solid surfaces submerged in a 2—5 % sulphite pulp suspension led to the following conclusions (1):

1. The resin is deposited at the pressure side of stationary solid surfaces and at the leading side of mobile solid surfaces in the pulp system — most rapidly where the shear forces are strongest. If the deposition surface is porous, e.g., a woollen felt, the resin accumulates where it has deposited. If the deposition surface is smooth, e.g. a metal surface, shear forces cause the deposited resin to flow along this surface. Part of this resin may eventually flow off again, especially where it must flow over a sharp edge; the remainder then accumulates at the trailing (or leeward)

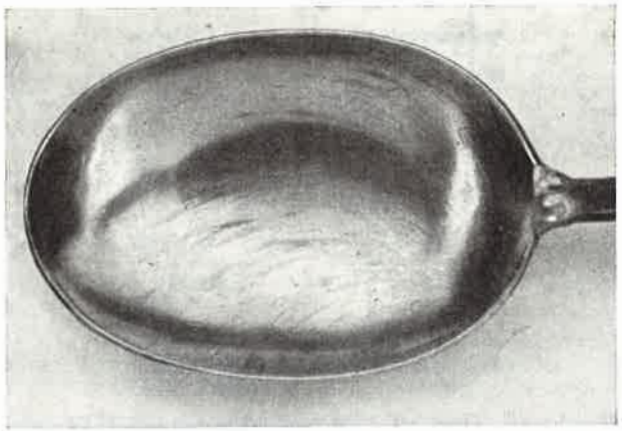

Figure 1. Concave inner surface of a spoon employed as the leading side of an exchangable stirrer blade of a pulp impeller. The initial resin deposition takes place at this leading surface, and later shear forces force the resin to flow along the surface and leave typical flow tracks.

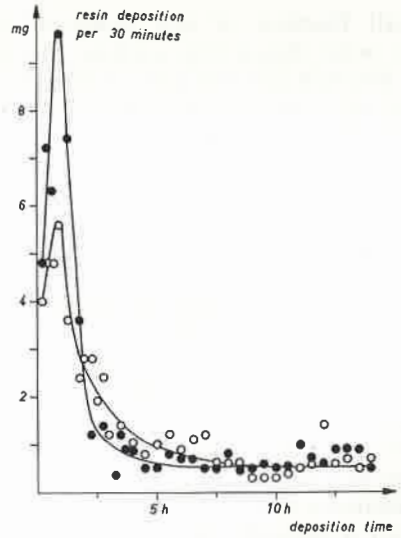

Figure 2. Resin deposition per unit time and per spoon blade versus time, using a stirrer with four blades. One blade exchanged at each point plotted. Two different experiments.

side of the body. *Figure 1* shows the pressure side of a spoon employed as a stirrer blade in the pulp suspension. Tracks of deposited resin indicate the pattern of pulp flow along the deposition surface.

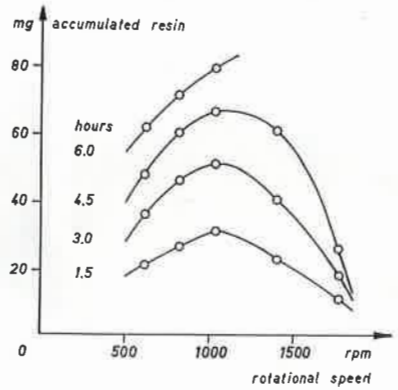

Figure 3. Total resin accumulation on copper stirrers versus the rotational speed of the stirrer. The total resin accumulation given for various deposition times on a copper propeller that was replaced every 1.5 hours.

2. Only a small fraction of the easily accessible resin is deposited on the solid deposition surface. Among the factors determining this amount are the area of the deposition surface within the system, its reactivity and finally its ability to collect the deposited resin. The major part of the resin coagulates in the pulp suspension, whereupon the stability of the remaining colloidal resin in this pulp system is increased. *Figure 2* illustrates how the resin deposited per unit time decreases from a rapidly achieved maximum to a very low value. This low value partly depends on the velocity with which additional resin particles are liberated by mechanical action from parenchyma cells in the pulp suspension.

3. The amount of resin that accumulates at a smooth surface falls off rapidly with increasing stirring speed as illustrated in *Figure 3*. The reason is that resin deposited again flows off, and more rapidly with increasing shear forces.

4. Any increase in the temperature of the system lowers the viscosity of the resinous matter. It thereby favours the flow of resin along and off a smooth deposition surface. *Figure 4* illustrates how the accumulation of resin on a metal surface falls off rapidly, while the accumulation of resin on a woollen felt increases with increasing temperature. On a smooth solid surface the effect of the lower resin viscosity predominates. On the porous surface, the woollen felt, the expected increase in the coagulation rate of the unstable hydrophobic resin colloid with increasing temperature is decisive.

5. As might be expected, the accumulation of resin varies with

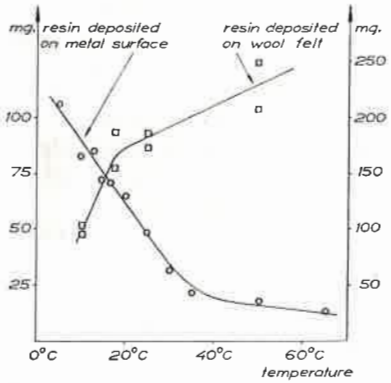

Figure 4. Accumulated resin versus pulp stock temperature in separate experiments with copper and with woollen felt as deposition surfaces. Both experiments refer to a 4 % sulphite pulp suspension and a total time of 6 hours. The resin accumulation on the woollen felt refers to 2 felt-covered spoons and a 400 gram pulp sample. The resin accumulation on the copper surface refers to a copper propeller replaced every 1.5 hours and a 200 gram pulp sample.

the chemical composition of the solid deposition surface. On a hydrophobic surface such as glass, the deposition is negligible under the model conditions (shear forces) in which the experiments were performed. Thus, the pulp suspension could be contained in glass cylinders, in which solid deposition surfaces in the form of vertical baffles were exposed to it. On metal surfaces the resin accumulation increases in the order: chromium, aluminium, stainless 8—18 steel, zinc and copper. This order is in agreement with the relative reactivities of these metals with fatty acids in water and with the relative amounts of fatty acids absorbed on these metals from organic solvents at equilibrium (2) (3) (4) (5). Especially metallic copper reacts rapidly at room temperature with fatty and resin acids. Accordingly, copper soaps are found in the resin that has accumulated on copper surfaces. The formation of a monofilm of metal soap is believed to be the primary step in resin deposition at solid surfaces in pulp systems.

Pitch Control by the Stabilization of Resin Particles

Paper mills have a rather closed white water system and resin particles cannot be washed from the pulp stock in the paper mill. They have to be removed from the system with the paper produced. A method of stabilization has to be selected to promote this resin disposal (6). For this purpose the negative surface

charges of pulp fibres are very useful. This negative surface charge originates in the carboxylic groups of hemicellulose components. Sulphite pulp has additional negative surface charges due to its residual lignosulphonic acid groups. To efficiently retain the resin particles in the wet web produced on a paper machine, they should then be stabilized with positive charges.

Surface charges on the resin particles can be produced either by the ionization of resin components or by the absorption of ions from the solution. Because a high surface tension favours the consolidation of the wet paper web, surface active agents cannot be used in paper mill systems except those producing special paper types. Thus the ions intended for absorption on resin particles have to be non-surface active polyvalent ions or polyions. To attract polycations or polyvalent metal ions, possibly with a subsequent attraction of polyanions, the carboxylic groups of the resin and fatty acids within the resin particles are employed. This mechanism is fundamental for resin stabilization and pitch control methods.

A certain amount of resin stabilization can result from the introduction of additional hydrophilic groups during the land storage of barked pulpwood. These additional hydrophilic groups arise from the autoxidation of resin components as well as from the hydrolysis of fatty acid and resin acid esters (6) (7) (8).

Anionic resin stabilization has been practised, especially earlier when paper mill white water systems were more open. The method employed was to add various sodium polyphosphates (9) (10) (11) (12) or certain types of condensed naphthaleneformaldehydesulphonic acids (10) (13) combined with a limited addition of aluminium sulphate or calcium salts. The stabilization achieved can be understood to result from a primary absorption of multivalent metal ions to produce metal salts on the resin particle surfaces followed by the absorption of a layer of the added polyanion. As an additional effect, the polyanions added may be adsorbed at active metal surfaces of paper machine parts and thereby reduce the pitch deposition on these surfaces. With this anionic resin stabilization the resin particles will accumulate in a closed white water system and thereby maintain a certain risk of heavy coagulation and pitch deposition.

Pitch control by positive charges employs the acid components on the resin particle surface either for the absorption of polycations, e.g., low molecular weight melamine and urea resins, or for reaction with cationic amines or polyvalent metal ions and excess absorption of these cations. Polyvalent metal ions are by far the least expensive of these cations. Thus aluminium sulphate has been extensively used as an inexpensive low corrosion pitch control agent. The underlying reaction is the formation of aluminium soaps of fatty and resin acids (HR) at the

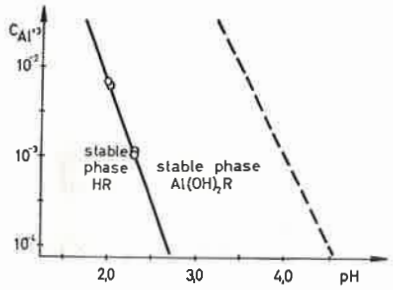

Figure 5. The stability limit for the solid phases of abietic acid (HR) and aluminium monoabietate ($Al(OH)_2R$) in aluminium salt solutions. At the border-line both solid phases co-exist at equilibrium. The dotted line refers to the aluminium perchlorate solutions in which abietic acid was dispersed at the beginning of the experiments.

surface as well as in deeper layers of the particles according to:

$$HR + Al^{+3} + H_2O \rightarrow Al(OH)_2R + 3H_2O^+$$

At water-air interfaces this reaction has been shown to take place within the pH range of 4—6 for various resin and fatty acids (14) (15) (16) (17). The reaction mechanism in a dispersed phase in water can be proved in the following way (18). Freshly precipitated abietic acid washed by decantation was dispersed in 0.003—0.03 molar aluminium perchlorate solutions. When the dispersion was stirred at room temperature, the pH and the aluminium ion concentration of the solution fell during a number of days. When the stirring was carried out during five days at 90°C in a closed bottle, an apparent equilibrium resulted. If an excess of aluminium perchlorate was present, the composition of the solid abietic acid phase changed into one close to that of aluminium monoabietate according to ash analysis. The product was soluble in chloroform but not in acetone, as is true for the monoabietate (19). If, instead, an excess of abietic acid was dispersed in the perchlorate solution, an equilibrium was obtained in which abietic acid and aluminium monoabietate are considered to coexist as separate solid phases. In this case the pH and pAl in this solution were determined by the solubility products of the abietic acid and the aluminium monoabietate. Such data when plotted in a pH-log($C_{Al^{+3}}$) diagram yield a straight border-line giving the equilibrium conditions at which the acid and the aluminium monosoap co-exist in the solid phase. The plot of pH versus log $C_{Al^{+3}}$ derived from the experimental measurements after a subsequent five-day reaction at 20°C is shown in *Figure 5*. To the left of the border-line only abietic acid, and to the right only aluminium monoabietate

can occur in the solid phase. This diagram is in essential agreement with the results of *Ekwall* and *Bruun* on the formation of aluminium monosoaps at the water-air interface (14) (15) (16) (17).

With a view to the use of aluminium sulphate for pitch control in paper mills important conclusions can be drawn from this diagram. To make possible an absorption of excess trivalent aluminium ions on the resin particles, it is necessary to maintain equilibrium conditions for a solid phase of aluminium monosoaps. Naturally, as a result of the complexity of the resin and fatty acids present in wood resin, the border-line of Figure 5 outlines only very approximately this pH/pAl^{+3} limit for paper mill systems and pitch control.

For highly closed paper mill systems, which are completely emptied only once a week or so, the surface reaction between resin and fatty acids and aluminium ions continously lowers the pH of the white water if a constant amount of aluminium sulphate is added per ton pulp. There is, however, a definite lower pH limit as regards paper quality and machine corrosion. Therefore the dosage of aluminium sulphate per ton of pulp usually is varied in paper mills in order to produce a pre-determined lower pH limit. This means that for pitch control there is available a varying aluminium ion content in the white water system which slowly decreases toward the end of the week. For this reason, combined addition of alkali and aluminium sulphate was investigated for pitch control (18). It was found that even in pulp flow model systems this combined addition of alkali and aluminium sulphate gave an immediate pitch control improvement as compared with a corresponding pure aluminium sulphate addition. Besides a lower resin deposition on metal and woollen felt, a rapid drop in finely dispersed resinous matter in the pulp suspension white water was apparent (18). A partial coagulation of resin particles on pulp fibres during the charge reversal on addition of aluminium sulphate subsequent to alkali may be the explanation. In practical application it is recommended to use from 0.05 to 0.2 % sodium hydroxide and from 0.8 to 1.5 % aluminium sulphate calculated on the weight of dry pulp. The order of addition of the two chemicals appears to be of little importance. The main advantage is the possibility of maintaining a constant level of aluminium ions at a high enough white water pH. Instead, the sodium hydroxide addition may be varied as governed by a continous white water pH meter to keep the pH at the predetermined value.

By following the principles reported here, it is possible to understand the main chemical aspects of pitch control and the use of pitch control agents in paper mills as surface chemical agents for the charge stabilization of resin particles.

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Surface Tensions and Wetting Phenomena of Solid and Molten Phases

Metallurgical Laboratory, Institute of Technology, Otaniemi, Finland.

M. H. Tikkanen

A review of the literature on surface chemistry shows that nearly all of the experimental research has been limited to water solutions. This does not mean, however, that corresponding phenomena are not observed in other kinds of systems. On the contrary, it is easy to show that innumerable heterogeneous systems exist where wetting phenomena have a decisive significance. These phenomena actually have their counterparts in systems containing molten and solid phases at high temperatures.

Research on the surface chemistry of molten metals and slags is yet quite young. The greater part of the papers have been published after 1950, and they are rather few in number. This is due partly to practical difficulties associated with measurements at high temperatures and partly to our insufficient knowledge of the structures of melts. It is evident, however, that the rapid technical development of the metallurgical industry will in the near future lead to much more intensive research in this field.

Measuring methods

The necessity of working at high temperatures greatly limits the selection of suitable conditions. Great difficulties are always experienced when working at temperatures above 1000°; these are partly due to temperature differences in different parts of the system and partly due to chemical reactions between different components of the system under study. Therefore there are only few methods suitable for measuring the surface tensions and the wetting properties of systems at high temperatures. Of these methods the sessile drop method is most frequently used. It is possible to measure by this method in many cases both the wetting properties and the surface tension of a molten phase at the same time. In Fig. 1 the principle of the measurement of wetting power is illustrated. The actual quantity measured is the con-

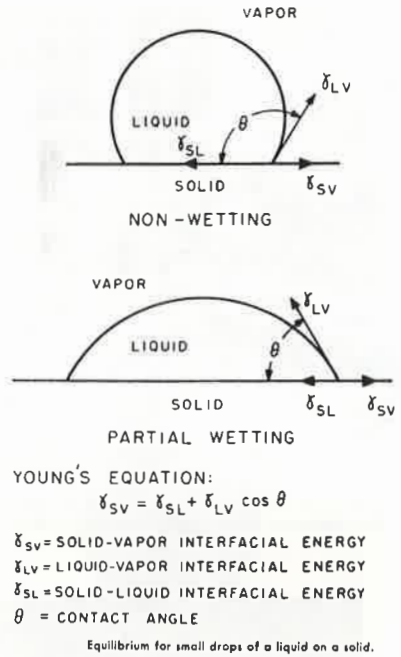

Fig. 1. Schematic drawing of the wetting of a solid support by a molten drop.

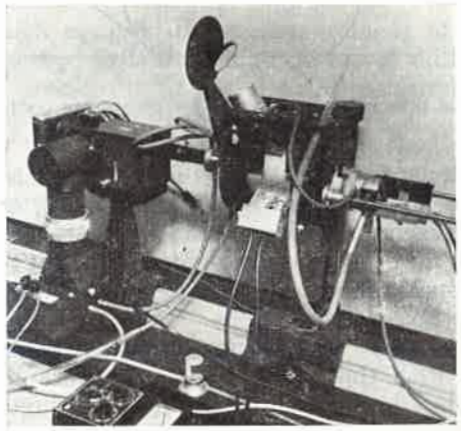

Fig. 2. High-temperature furnace (Leitz, Germany) for photography of specimen contours inside the furnace. Max. temperature 1750°C.

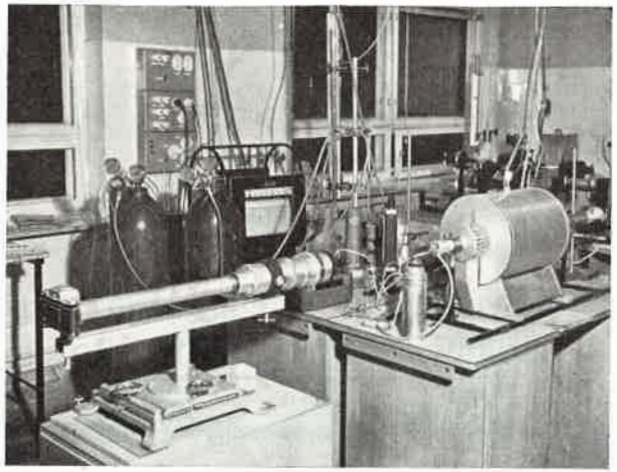

Fig. 3. High-temperature furnace for photography of specimen contours inside the furnace. Max. temperature 1550°C.

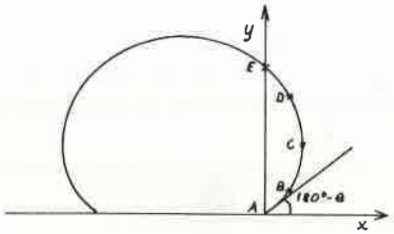

Fig. 4. The principle of method I for measuring contact angles.

tact angle. Generally speaking, the liquid wets the support material if the contact agle is less than 90°C, and vice versa. This kind of division of different materials into wetting and non-wetting types may not be the right one, and it certainly would be better to speak about different degrees of wetting and leave out terms like non-wetting.

The apparatus used in such measurements is shown in Fig. 2. It is possible with this apparatus to photograph the contours of a droplet placed on a supporting material directly in the furnace. As the magnification of the commercial instrument (Erhitzungsmikroskop, Bauart Leitz) is twentyfold, it is necessary to use very small droplets (2—3 cu.mm.). In some cases this can be difficult and it would be preferable to use an apparatus with a lower magnification (Fig. 3).

The measurement of the contact angle can be carried out in different ways. In the newest apparatus an auxiliary device may

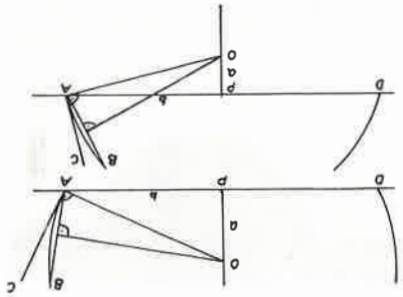

Fig. 5. The principle of method II for measuring contact angles.

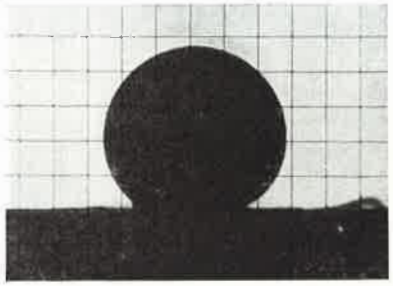

Fig. 6. An almost non-wetting drop on a solid support (molten Co on CaO).

be attached which permits direct measurement of the contact angle. As this method calls for a high degree of skill and experience, the usual practice is to perform the measurements on enlarged photographs in one of the following ways.

Fig. 4 shows the principle of the first method. The coordinates of, e.g., the points A (x_1, y_1), B (x_2, y_2), C (x_3, y_3) D (x_4, y_4), and E (x_5, y_5) are measured and the equation $Y = f(x, y)$ of the curve passing through these points is derived.

The contact angle is then calculated from

$$\Theta = 180° - \text{arc tang } y^1$$

where y^1 is the first derivative of f(x,y) at point A. In order to attain the highest precision, it is necessary to use a calculating machine.

Fig. 5 shows the principle of the second method. The center of the arc AB is determined and the perpendicular OA is drawn. The contact angle (PAC) is then

$$\Theta = 90° \pm \text{arc tang } a/b$$

where a = OP and b = AP = 1/2 AD.

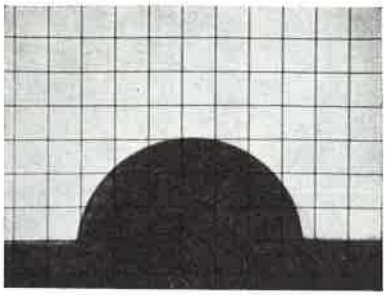

Fig. 7. A moderately wetting drop on a solid support (molten Ni on WC).

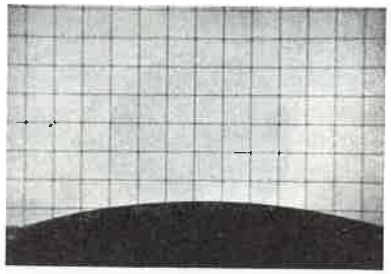

Fig. 8. An almost completely wetting drop on a solid support (molten Ni—Mo alloy on TiC).

The surface tension of the droplet (against the gas phase) when the contact agle is less than 90° can be calculated with the aid of the well-known Adams-Basworth tables after measuring the length of the greatest horizontal distance and the distance between the base line and the top of the droplet.

Typical contours are shown in Figs. 6—8 for molten droplets whose ability to wet the support material is very weak, moderate and strong.

Surface tension

A molten droplet on a support may react with the gas phase and with the solid phase. This can lead to many complications, the number of which will increase with the number of the components in the system. Therefore this survey is intentionally limited to systems composed of molten metals and solid oxides.

Molten metals dissolve appreciable quantities of many non-metallic elements. In this connection it is important to point out that some of the non-metallic elements, especially oxygen and sulphur, exhibit a high surface activity when dissolved in metals. Fig. 9 shows how small amounts of oxygen and sulphur

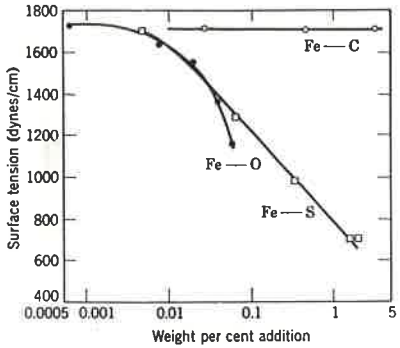

Fig. 9. The influence of small amounts of O, S and C on the surface tension of molten iron [1].

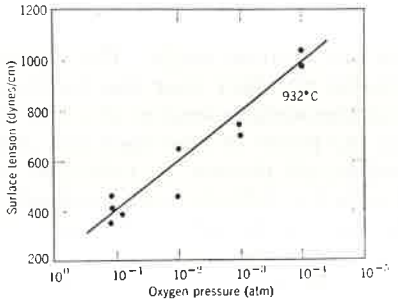

Fig. 10. The influence of dissolved oxygen on the surface tension of solid silver [2].

decrease the surface tension of molten iron [1]. Fig. 10 shows further that this effect is not limited to systems of molten metals, but is observed in solid metals too[2]. Thus the surface tension of solid silver diminishes rapidly when oxygen is dissolved in the solid metal. In this special case the oxygen content is deduced indirectly from the partial pressure of oxygen in the gas phase instead determining the oxygen content directly.

These two examples show the importance of the purity of the gas phase when determining wetting properties at high temperatures. Usually the measurements are made in an inert atmosphere, i.e. in vacuo, argon or nitrogen. When these non-reactive gases are used they have to be deoxidized very carefully. In most cases the use of a vacuum would be preferable, but this is limited by the difficulty of devising suitable apparatus.

Wetting

The measurement of the surface tension in a neutral atmosphere is quite simple compared with the measurement of wetting

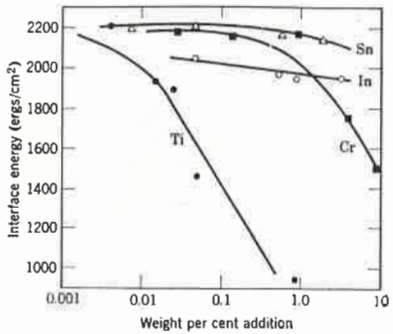

Fig. 11. The influence of different alloying elements in Ni on the wetting of solid Al_2O_3 by molten Ni. Note that a decrease in interfacial energy corresponds to an increased wetting of the oxide by Ni.

properties, i.e. of the contact angle. The opinion of the author is that this is due to the fact that the wetting ability is not a fixed property like the surface tension of a pure liquid in a neutral atmosphere. It is the result of chemical and physical interaction between solid and liquid phases. In principle, the contact angle value should always be definite and constant when the system is at true equilibrium. This is, however, not always possible to attain as the reactions in the solid phases are often very slow.

There are many different opinions on the ultimate cause of the wetting of a solid oxide support by a molten metal. Our knowledge of these problems is unfortunately too scanty to make it possible to present a satisfactory theory of wetting. One thing, however, is certain in principle. If there is no chemical interaction (i.e. affinity) between the molten and solid phases, there will be no wetting either. With increased chemical interaction, the wetting will be in some, not yet known, relation to other properties of the system.

Experience shows that the wetting of chemical stable oxides (Al_2O_3, CaO, MgO) is especially by non-reactive molten metals low when it is determined in a neutral or reducing atmosphere. This is now ascribed to a deficient affinity between the two phases. Physically this can be interpreted by assuming that the oxide surface contains almost only negative oxygen ions, which exert a repulsive effect on the negative electron cloud of the metallic phase.

The wetting will be increased if the oxide reacts with the molten metal, and vice versa. Such reactions are, however, difficult to explain, as is often usual for reactions in the solid state. A typical example is shown in Fig. 11, where the influence of small amounts of Ti in molten Ni on the wetting of Al_2O_3 by Ni

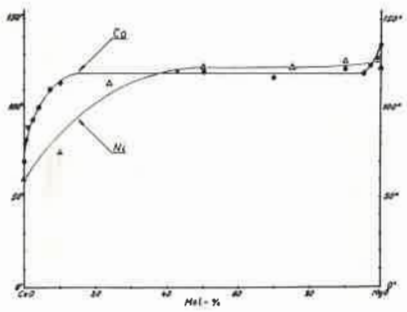

Fig. 12. The influence of dissolved MgO in CoO on the wetting solid oxide solution by molten Co. Temp. 1500°C, nitrogen atmosphere. Note that this effect occurs also with Ni.

is presented [3]. In this special case the wetting ability is expressed in terms of the interface energy (i.e. the surface energy of Ni in contact with Al_2O_3). This influence of Ti depends on its high affinity for oxygen, which results in a reaction between Al_2O_3 and the dissolved Ti, which reaction proceeds to only an exceedingly small extent in the system Ni—Al_2O_3.

The reactivity of solids depends on the existence, the nature and the number of structural defects they contain. It is important to note that these defects are, directly or indirectly, reaction conponents. In most cases the reactive oxides are non-stoichiometric compounds containing an excess of metal or non-metal (n and p types).

In the following some results for the system Co—CoO—MgO, the purpose of which is to illustrate the chain of reasoning indicated above, will be reviewed. Fig. 12 shows how the wetting by molten Co of a supporting plate of CoO containing different amounts of MgO in solid solution diminishes (i.e. the contact angle increases) with increasing MgO content. It is known that CoO has an ionic lattice and that it is semiconductor of the p type, that is, an oxide with excess oxygen, the formation of which from stoichiometric CoO can be expressed as follows:

$$1/2O_2(g) + 2\ Co^{2+} \rightleftharpoons O^{2-} + 2\ Co^{3+} + \square\ Co^{2+} \qquad [1]$$

Thus there will be in the lattice two Co^{3+} ions and one cation vacancy ($\square\ Co^{2+}$) for every O^{2-} ion in excess. In this case it is more rational to speak of a metal deficit and cation vacancies than of an oxygen excess as all the experimental results suggest that the anion lattice is perfect in this kind of oxide and that the defects result from changes in the cation lattice. The deviation from the stoichiometric composition and the associated electronic conductivity (i.e. the amount of Co^{3+}) of CoO are in thermody-

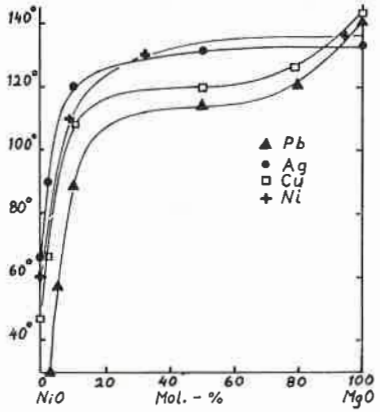

Fig. 13. The influence of dissolved MgO in NiO on the wetting of the solid oxide solution by molten Pb, Ag, Cu[5], and Ni[6].

namic equilibrium with the partial pressure of oxygen as shown in Eq. [1]. If such an oxide comes into contact with metallic Co this equilibrium will change as follows:

$$Co(1) + 2Co^{3+} + \square\, Co^{2+} \rightleftharpoons 3\, Co^{2+} \qquad [2]$$

This means that the number of Co^{3+} ions and cation vacancies will diminish and the composition of the oxide will chang to more stoichiometric values. The variation of the contact angle presented in Fig. 12 for pure CoO is the result of this kind of interaction between molten Co and solid CoO.

The addition of MgO to give a solid solution results in a marked increase in the contact angle. This effect is a consequence of a diminished reactivity of CoO with metallic Co resulting from the addition. This has been verified for other reactions [4]. The Mg^{2+} ions in solid solution in the CoO lattice are evidently able to change the defect equilibrium by interacting with the different cations in the ionic lattice [5].

Other examples of the same kind are shown in Fig. 13.

Practical applications

Wetting phenomena are particularly important in metallurgical processes. Thus in steel melting furnaces (as in all metal melting furnaces) the composition of the molten metal is changed by contact with molten oxide slag. During the oxidation period there is a flow of oxygen from the molten oxide phase to the molten metal phase, where it reacts with dissolved carbon atoms to form gaseous carbon monoxide. In the same manner desulphurization is accomplished by changing the thermodynamic conditions in such a direction that a flow of sulphur from the metallic phase to the slag phase is possible. Reactions of this type are common for most metals. In all such heterogeneous systems the wetting interactions and simultaneously occurring chemical reactions between the different phases must be very intimately connected.

Many more practical examples could be presented. Among them are the enameling of steel (molten oxide — solid metal), reaction between molten metal and furnace walls (molten metal — solid oxide), the soldering of metals (molten metal — solid metal), the melting of glass (molten oxide — solid oxide), the structure of metals (solid metal — solid metal), the structures of the hard metals and cermets (molten metal — solid carbide or solid metal — solid oxide).

This short survey may have shown that there is a great *terra incognita* which abounds in interesting and important problems for students of surface chemistry.

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6. *Tikkanen, M. H.*, Jernkont. Ann. **147** (1963) :46

Berättelse över Finska Kemistsamfundets verksamhet under år 1962

(Avgiven vid mötet den 11 februari 1963)

Samfundet har under året sammanträtt till 6 ordinarie möten, nämligen den 12 februari, 12 mars, 9 april, 8 oktober, 12 november och 10 december. Närvarande har i medeltal varit 34 personer per möte. Den 14 maj anordnade Samfundet en exkursion till Printal Oy och Oy Medica Ab.

Vid Samfundets möten har följande föredrag hållits och meddelanden avgivits:

Fil.mag. *Fred Björksten:* Samband mellan peroxidasenzym och sköldkörtelhormoner.

Fil.dr *Kurt Ekman:* »Western larch» och arabinogalaktan.

Fil.dr *Camilla Juslén:* Om hjärtglykosidernas förekomst i naturen och deras egenskaper.

Fil.dr *Folke Koroleff:* Analys av havsvatten.

Fil.mag. *Kristian Lindroos:* Polyretan- den moderna skumplasten.

Prof. *Bengt Rånby:* Molekylär tolkning av polymerers mekaniska egenskaper.

Fil.mag. *Carl-Gustaf Spåre:* Om lökens tårframkallande ämnen.

Fil.lic. *Ebbe Still* och *Folke Ingman:* Grafiska metoder för bestämning av ekvivalenspunkter.

Docent *Henrik Wallgren:* Inverkan av alkohol på hjärnans metabolism.

Docent *Birger Wiik:* Meteoriterna — spånor från världsrymden.

Det elfte nordiska kemistmötet hölls i augusti i Åbo. Vid mötets öppningstillfälle höll prof. *Anders Ringbom* ett föredrag om »Mikromängder i kemin». I samband med mötet ordnades tre symposier. Ordförande för symposiet om cellulosakemi var prof. *W. Jensen* och ordförande för symposiet om ytkemi var Samfundets hedersledamot prof. *P. Ekwall.* Ett flertal av Samfundets medlemmar höll även kortare föredrag i de sex olika sektionerna vid mötet.

Under året har fyra (varav ett dubbelnummer) av Finska Kemistsamfundets Meddelanden utkommit. Det totala sidoantalet har varit 140.

Vid årsmötet den 10 december tilldelades docent *Ralph Gräsbeck* bergsrådet Alfthans pris för år 1962 för uppsatsen »Contributions to the Biochemistry and Physiology of Vitamin B_{12} and Intrinsic Factor» som ingått i Meddelandena n:o 3–4, 1961. Prisets storlek var 20 000 mk.

Under året har en av Samfundets medlemmar avlidit nämligen:

Fil.mag. *Bertel Geitlin.*

Nio medlemmar har avgått. Samfundet har invalt 6 nya medlemmar. Medlemsantalet är 386. Styrelsen har sammanträtt 7 gånger. Dess sammansättning har varit följande:

ordförande: fil.dr *Olof Forsander*
viceordförande: bitr. prof. *Jarl Gripenberg*
sekreterare: fil.dr *Tor-Magnus Enari*
medlemmar: prof. *Terje Enkvist*
fil.dr *Charley Gustafsson*
fil.lic. *Nils-Erik Saris*
fil.dr *Tor Smedslund*
prof. *Albert Sundgrén*
tekn.dr *Jacobus Sundman*

Samfundets funktionärer har varit:
kassör: fil.kand. *Karin Sandelin*
arkivarie: dipl.ing. *Anna Grönvik*
redaktör: fil.dr *Tor-Magnus Enari*

Revisorer har varit: fil.dr *William Forsman* och dipl.ing. *Paul Ålander* med fil.mag. *Holger Lönegren* som suppleant.

Samfundets valda representanter i Centralrådet för Finlands Kemister har varit prof. *Terje Enkvist* och tekn.dr *Jacobus Sundman.* Ordföranden, fil.dr *Olof Forsander* och sekreteraren, fil.dr *Tor-Magnus Enari* har varit självskrivna medlemmar.

Olof Forsander
ordförande

Tor-Magnus Enari
sekreterare

FINSKA KEMISTSAMFUNDETS MEDDELANDEN

Annonspris

på annonssidor	80:—
på sidor mot text	80:—
på bakpärmen	100:—

Prenumerationspris

i Finland	10:—
till utlandet	12:—

Annonser och prenumerationsärenden

Fil. mag. Karin Sandelin
Universitetets Virologiska institution
Fabiansgatan 24
Telefon 63 48 03

SUOMEN KEMISTISEURAN TIEDONANTOJA

Ilmoitushinnat

ilmoitussivuilla	80:—
tekstin vastaisella sivulla	80:—
takakannessa	100:—

Tilaushinta

Suomessa	10:—
Ulkomailla	12:—

Ilmoitus- ja tilausasiat

Fil. maist. Karin Sandelin
Yliopiston Virusopin laitos
Fabianinkatu 24
Puhelin 63 48 03

Helsingfors 1963, Frenckellska Tryckeri Aktiebolaget