

The Adsorption of n-Octadecylamine, n-Octadecanoic Acid, and n-Octadecyl Alcohol from Nonaqueous Solution onto Hydrated and Dehydrated Metal Oxide Surfaces

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ABSTRACT

A study has been made of the adsorption of the normal C₁₈ amine, acid, and alcohol from hydrocarbon solution onto freshly polished stainless steel, iron, nickel, chromium, and platinum surfaces as a function of substrate pretreatment. The pretreatment consisted of maintaining the polished surface for 3 hours in a helium or air environment at selected temperatures ranging from ambient to 320°C. Isolation of the monolayer-covered surface was accomplished by the method of retraction, and the degree of coverage was determined by measuring the contact angle. Treatment of the metal surface at temperatures from 25 to 200°C resulted in a more-or-less continuous decline in ability to adsorb a close-packed monolayer of the amine. Above 200°C, however, amine adsorption increased with increasing pretreatment temperature except on platinum. The regain in amine adsorption is believed to be connected with oxide film growth.

In anhydrous solution neither the alcohol nor the acid formed a close-packed monolayer. On the other hand, it was possible to obtain a monolayer and even crystallites of octadecanoic acid when the substrate was heavily hydrated and the adsorbate solution was saturated with water.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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THE ADSORPTION OF n-OCTADECYLAMINE, n-OCTADECANOIC ACID,
AND n-OCTADECYL ALCOHOL FROM NONAQUEOUS SOLUTION
ONTO HYDRATED AND DEHYDRATED METAL OXIDE SURFACES

UNCLASSIFIED

INTRODUCTION

It has been repeatedly found that the presence of water on the surface of metals and metal oxides substantially enhances the adsorption of alkyl carboxylic acids and other amphipathic solutes from hydrocarbon solution (1-5). It was generally found that water physically adsorbed on a metal oxide surface assists the acid in forming the corresponding metal soap. In contrast, the adsorption of dinonylnaphthalene sulfonic acid from hydrocarbon solution onto clean, polished steel was not found to be affected by the presence of water, although the alkali and alkaline earth metal soaps of this acid formed closer packed monolayers from water-saturated solution than they did from anhydrous solution (6). The effect of water on soap adsorption (for which chemisorption seems unlikely) was attributed to the hydration of the sulfonate-cation ion-pair. There is also evidence from surface potential studies that water is involved in the bonding of organic amines to metal ions (7-9).

The work reported here examined the influence of water on adsorption at oil/metal interfaces by studying the effect of the progressive dehydration of polished metal surfaces on their ability to adsorb octadecylamine, octadecanoic acid, and octadecyl alcohol from hydrocarbon solution. These particular compounds were selected because they represent both acidic and basic functional groups; and since the organic chains are the same, differences in their adsorption on a given substrate can be related to differences in the behavior of the polar end. Adsorption at the oil/metal interface was followed by determining the contact angles for various test liquids on the adsorbate-coated substrate; the substrate was isolated from the solution by the method of retraction (10).

EXPERIMENTAL PROCEDURE

Materials

The metals studied were Armco iron (99.8% Fe), nickel (99% Ni), stainless steel (18% Cr + 8% Ni), and chromium (99% Cr). The indicated purities are the minimal values given by the manufacturers. High-purity platinum was also studied, but its exact analysis was not known. The specimens were in the shape of either small disks or plates with the edges and faces of each piece ground smooth and one face polished to a mirror finish. Before being put into adsorbate solution, the entire specimen was cleaned by abrading on a metallographic wheel with an alumina-water slurry or with diamond powder suspended in water. Residual abrasive was removed by holding the piece against the uncharged cloth and flooding with water. Inspection of the mirror surface by bright- and dark-field microscopy did not reveal any embedded alumina. Electron microscopy of cast and shadowed replicas of the steel surfaces at magnifications up to 25000X showed only an occasional inclusion. The embedding of abrasive was minimized by holding the metal plate lightly against the cloth and using only a dilute abrasive slurry. The polished specimens were washed with distilled water, and the surfaces were presumed free of organic contamination if the water maintained a zero contact angle as it drained and evaporated.

The adsorbates were reagent-grade octadecylamine (mp 51-52°C), octadecanoic acid (mp 68-70°C) and octadecyl alcohol (mp 59°C). They were used as obtained from the supplier. The principal solvent from which these materials were adsorbed was isopropylbiphenyl, which proved to have a high enough surface tension to be oleophobic to all of the monolayers formed. This solvent, the other solvents used (bicyclohexyl and hexadecane), and the organic liquids used for contact angle measurements were reagent-grade materials from which polar contaminants had been removed by percolation through activated adsorbents.

Methods

The cleaned metals were subjected to dehydrating conditions in a glass cell evacuated to 0.3 to 0.4 mm Hg at temperatures ranging from ambient to 320°C. In order to promote water removal and to maintain constant pressure from one experiment to the next, helium that had been dried over molecular sieve granules was continuously leaked into the cell. Grease connections were avoided by using O-ring joints with Viton or Teflon O-rings. The chamber containing the specimen fitted into a small heating jacket, and the temperature was recorded continuously from a thermocouple placed in a hole drilled into the side of each metal specimen. The metal was guarded from organic contamination during the dehydration process by having the helium enter the cell through a short column of molecular sieve adsorbent and by placing a similar column at the opening to the vacuum line. After the appropriate dehydration period and while continuing the helium flow, the cell was cooled to ambient temperature (~25°C), and the adsorbate solution was run into the specimen chamber. The metal was kept in the solution overnight; tests showed that no further change occurred beyond that time.

The film-covered surface was isolated by removing the specimen from the solution and allowing the liquid to retract. Contact angles were made on the dry mirror surface using the generating solution itself or various other organic liquids. The contact angles were determined by the sessile-drop method at 25°C with a goniometer telescope. The surface tensions of the liquids were measured at 25°C by the ring method.

RESULTS

A systematic study was made of films of octadecylamine adsorbed from isopropylbiphenyl onto polished surfaces of iron, nickel, chromium, and stainless steel after the metal substrate had been heated to various temperatures. The contact angles exhibited by the adsorbate solution on the adsorbed films are plotted in Figs. 1 and 2 against the substrate pretreatment temperature. The results were essentially the same for amine concentrations ranging from 0.1 wt-% to a nearly saturated solution. The choice of isopropylbiphenyl as the solvent was experimentally convenient because its high surface tension caused this liquid to retract readily from almost all of the monolayers encountered. Although the less oleophobic monolayers could not be isolated from bicyclohexyl and hexadecane, the films from which these solvents did retract had the same wetting properties as did corresponding films obtained from the biphenyl solvent. It was consistently found that at any given temperature heating the substrate for longer than 3 hours before adsorption did not result in any further change in the character of the adsorbed film.

Figures 1 and 2 show that the patterns of behavior for the different metals were similar except in the case of platinum. That is, the contact angle decreased progressively with increasing pretreatment temperatures up to some point between 150 and 200°C. For pretreatment temperatures above this range the contact angle tended to increase. The exact temperature at which the change in contact angle reversed and the extent of this reversal depended upon the metal substrate. The experimental data were

easily reproducible except for the results on nickel, for which the data above 150°C had to be represented as a band. The results on platinum did not fit the general pattern established for the other substrates. The data in Fig. 2 show that for this metal the contact angle decreased markedly for pretreatment temperature just above ambient and did not change again through the temperature range studied.

The differences in contact angle were not due to changes in the roughness of the surface. Microscopic examination indicated that in general the topography of the metal specimens was unaffected by the heating treatment. An increase in the crystallinity of the surface was noted for the iron and steel specimens when heated above 200°C, but this increase in microroughness would decrease the contact angle rather than increase it.

In order to confirm that the different contact angles of the generating solution correspond to differences in packing of the octadecylamine, the critical surface tension (γ_c) was determined for the adsorbed films that had formed on steel and iron. Zisman (11) has established that the critical surface tension is a characteristic property of nonpolar surfaces and a useful index of differences in the packing of oleophobic monolayers adsorbed on solids. In the case of straight-chain compounds such as octadecylamine the critical surface tension for a tightly packed monolayer is 22 dynes/cm using the n-alkanes as the wetting liquids (11). If γ_c is greater than this value, the adsorbate must be considered less than close packed.

The wetting data for the n-alkanes have been plotted in Fig. 3 and show that optimum packing was obtained for the octadecylamine monolayer on iron dried at 25°C ($\gamma_c = 22$ dynes/cm) but that the degree of packing was less when the steel had been pretreated at 160°C ($\gamma_c = 27$ dynes/cm). Iron heated to ~300°C adsorbed a monolayer that was slightly less than close packed ($\gamma_c = 23.5$ dynes/cm). These differences in adsorbate packing parallel the changes in the contact angles shown in Fig. 1 for the adsorbate solution on the isolated films.

In view of the observed relation between amine adsorption and substrate pretreatment, an effort was made to determine if the changes in solute adsorption were due entirely to dehydration or whether other factors such as metal oxidation or the choice of abrasive also contributed to the observed behavior. In order to determine if oxidation of the substrate played a role, the dehydration of iron and steel was carried out using an air leak in place of the helium. The data for these experiments are presented as solid points in Fig. 1. The substitution of air for helium had no effect on amine adsorption when iron was pretreated below 200°C but did allow the substrate to adsorb a more closely packed monolayer when heated above this temperature. A curious aspect of the effect of heating in air above 200°C was that even though the abilities of the surfaces to adsorb amine differed significantly, the thickness of the oxide film on the iron substrate was essentially the same whether heated in air or helium. Oxide thickness was judged from the interference colors produced (12). Thus, the data points in Fig. 1 obtained on iron heated at

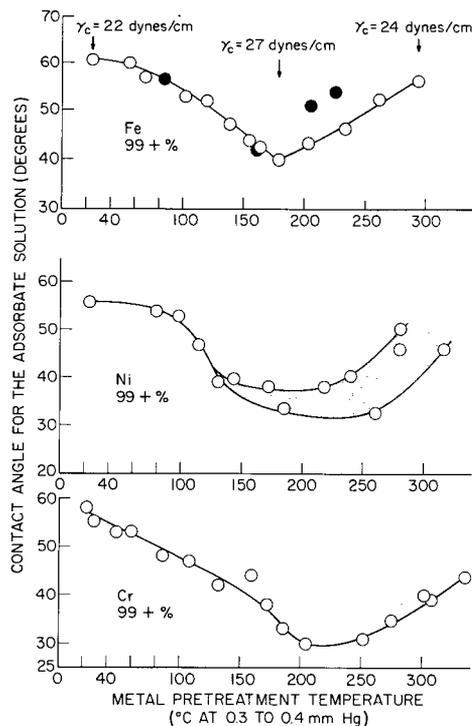


Fig. 1 - The change in adsorbate solution contact angle with substrate pretreatment temperature for octadecylamine monolayers adsorbed from isopropylbiphenyl solution onto iron, nickel, and chromium (filled circles indicate substrate pretreated in dry air instead of helium)

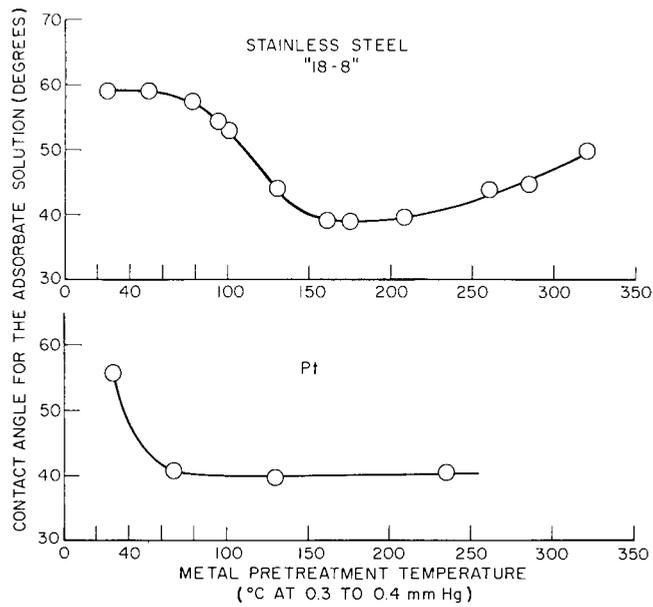


Fig. 2 - The change in adsorbate solution contact angle with substrate pretreatment temperature for octadecylamine monolayers adsorbed from isopropylbiphenyl solution onto stainless steel and platinum

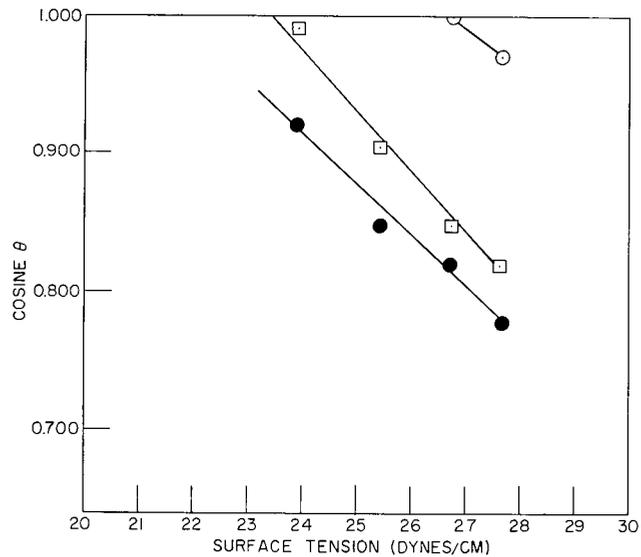


Fig. 3 - Contact angle versus surface tension for n-alkanes on octadecylamine monolayers for iron substrates pretreated at 25°C (•), at 160°C (o), and at 300°C (□)

205°C in air and in helium are in each case for surfaces having a light straw tint corresponding to an oxide coating of about 450Å; yet the contact angles differed by 7°. Clearly, there was oxygen present in the helium stream sufficient to produce an oxide film comparable to that formed in air. However, the oxide formed in the helium was less capable of adsorbing amine presumably because it was formed at a substantially lower partial pressure of oxygen than the oxide formed in air.

The use of diamond dust as the polishing powder in place of alumina had the effect of reducing the ability of the metal substrate to adsorb amine, an effect which was found to be associated with the alkaline nature of the alumina-water polishing slurry. The data obtained on nickel that had been diamond polished are given in Fig. 4. At pretreatment temperatures from ambient to 150°C the amine monolayers formed on the diamond-cleaned surfaces had lower contact angles and thus were less closely packed than the monolayers formed on alumina-polished surfaces. For pretreatment temperatures above 150°C, any differences in the two sets of results were masked by the scatter in the data. It was found that the important difference between the two polishing powders was that the pH of the alumina slurry taken directly from the polishing cloth was relatively high, about 8.1, whereas the pH of the diamond slurry was 7.3. When the diamond slurry was made alkaline (pH = 10), the resulting nickel substrate could adsorb an amine monolayer nearly as well as when polished with the alumina. The solid data point in Fig. 4 shows this effect of the alkaline diamond polish.

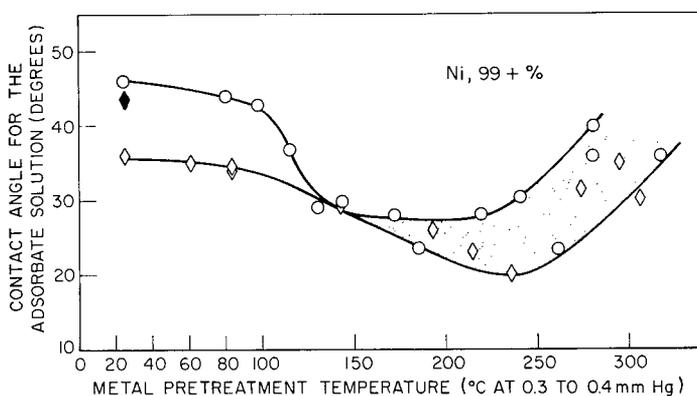


Fig. 4 - The change in adsorbate solution contact angle with substrate pretreatment temperature and polishing procedure for octadecylamine monolayers adsorbed from isopropylbiphenyl solution (O, alumina polishing powder; ◇, diamond polishing powder; ◆, diamond polishing powder made alkaline)

Efforts were made to determine if the inability of the dehydrated metal surfaces to adsorb a close-packed monolayer of amine could be reversed by exposure to moisture. The procedure was to first dehydrate iron plates at 180°C so that they would have a minimum tendency to adsorb amine. Then rehydration was attempted by (a) saturating the adsorbate solution with water, (b) by contacting the substrate with water vapor at various temperatures, or (c) by contacting the substrate with bulk water. Relatively severe conditions were necessary to achieve a significant increase in amine adsorption. The results on iron heated to 180°C and then placed in amine solution that had been saturated with water were the same as for the anhydrous solution unless the metal was

allowed to remain in the wet solution for more than 72 hours. After such an extended contact time, the monolayer gave a contact angle of 52° , which is 12° higher than obtained from the dry adsorbate solution but still less than the 60° which corresponds to closest packing. In another series of experiments dehydrated iron specimens were contacted for 3 hours with helium gas which had been saturated with water vapor at room temperature. Unless the metal surfaces were heated to over 140°C during contact with the wet gas, there was no significant increase in their ability to adsorb amine. Contact with bulk water at elevated temperature was most effective in restoring the ability of the metal to adsorb amine. Steel plates were dehydrated at 200°C and then placed in distilled water at room temperature and at 60°C . At the higher temperature it took only 1 hour in water compared with 50 hours at room temperature to regenerate the surface so that the amine monolayer formed had a contact angle of 55° . This is an increase of 12° over the contact angle on a monolayer formed in the absence of water on a steel plate dehydrated at 200°C .

Octadecanoic acid and octadecyl alcohol formed monolayers on polished iron that were considerably less oleophobic than the films formed by octadecylamine. Contact angles of the generating solutions are plotted in Fig. 3 as a function of substrate pretreatment temperature. The surface tensions of all three adsorbate solutions were identical, so the contact angle data are directly comparable regardless of which solution was used as the test liquid. The relatively low contact angles obtained on the films of acid and alcohol indicate that these adsorbates formed less closely packed monolayers than did the amine. For comparison, a dotted line corresponding to the amine data is included in Fig. 5. The octadecyl alcohol showed a small but distinct decrease in contact angle with increased pretreatment temperature until above 200°C the adsorbate solution completely wet the surface and would not retract. The octadecanoic acid was also poorly adsorbed but always formed a sufficiently oleophobic film to permit retraction. The results were unchanged for either adsorbate by increasing the solute concentration from 0.2% to nearly saturated solutions. Also, no detectable difference was ever produced by allowing the substrate to remain in contact with the adsorbate solution for over 72 hours. Results similar to those obtained on iron were also obtained on stainless steel and platinum. Nickel and chromium were not investigated in these adsorbate solutions.

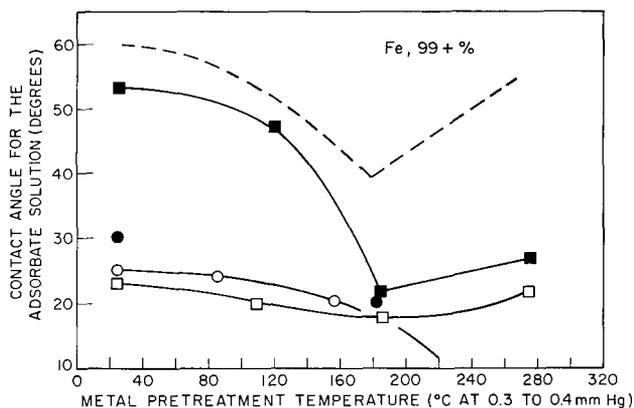


Fig. 5 - The change in adsorbate solution contact angle with substrate pretreatment temperature for octadecanoic acid, octadecyl alcohol, and octadecylamine monolayers on iron (C_{18} -acid, □ dry, ■ wet; C_{18} -alcohol, ○ dry, ● wet; C_{18} -amine, (---) dry and wet)

A remarkably greater adsorption of octadecanoic acid occurred when the adsorbate solution was saturated with water, a phenomenon not exhibited by either the amine or the alcohol. On iron substrates preconditioned between 25 and 180°C the wet octadecanoic acid solutions formed films comparable in oleophobicity to the films formed by the amine. However, the high contact angles indicated in Fig. 5 were not obtained if the metal was allowed to remain in the acid solution more than 1/2 hour. After contact times longer than this, retraction was erratic; and even on areas from which the liquid did retract, the test drop had irregular edges and contact angles were impossible to read. This erratic behavior is usually characteristic of highly rough surfaces. Indeed, dark-field microscopic examination revealed minute deposits over the surface as in Fig. 6. These deposits seemed to be more concentrated on some crystal grains than on others and also tended to concentrate along grain boundaries and along the micro-scratches that criss-cross the surface. The enhancement of acid adsorption by water relative to the dry adsorbate solution was not evident on iron surfaces heated above 180°C.

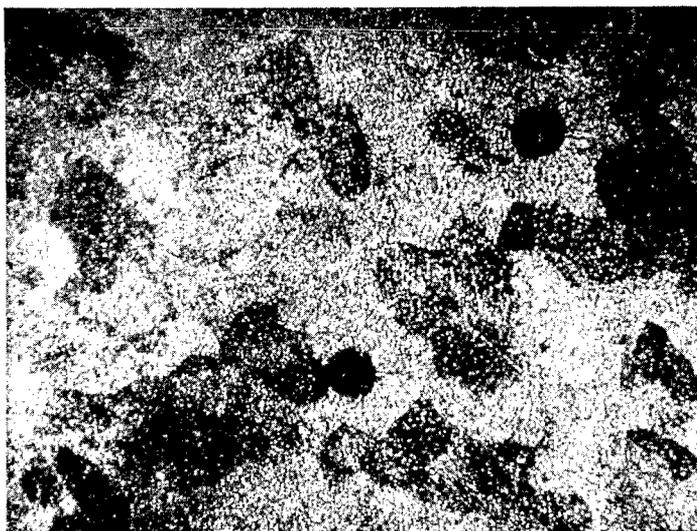


Fig. 6 - A dark-field photomicrograph of an iron surface isolated from a water-saturated solution of octadecanoic acid in isopropylbiphenyl

DISCUSSION

Octadecylamine

Clear evidence has been obtained here that adsorbed water plays a critical role in the adsorption of octadecylamine on polished metal surfaces. Whether the water is physically held or chemically combined is difficult to distinguish. Amine adsorption was generally characterized by the progressive change from close-packed monolayer formation on metals that had been dried at room temperature to less close packing on surfaces dried at higher temperatures. The temperature at which molecular packing appeared to reach a minimum varied somewhat for the different metals studied. When heated above this characteristic temperature, some of the metals regained their ability to adsorb amine. This regeneration appeared to be associated with changes in the oxide on the metal surface.

On the basis of the experiments reported here and the known behavior of oxide films on metals it is possible to construct a reasonable picture of the oxide substrate changes that were responsible for the observed changes in amine adsorption. It seems likely that the polishing process produces a heavily hydrated surface containing both metal oxide and hydroxide. Hydroxyl groups would certainly be introduced by the alkaline alumina slurry, and because of the low work function of freshly abraded metal, hydroxyl groups can also be introduced into the surface layer by a free radical decomposition of water (13). These hydrated surfaces may bear some chemical resemblance to the hydrous oxide gel precipitates. Fontana has given electron diffraction evidence that a hydrous oxide forms on stainless steel surfaces abraded in air (14). The isobaric dehydration to which the polished plates were subjected undoubtedly produced a progressive loss of both physically and chemically bound water from the surface. In view of the fact that the greatest decline in ability to adsorb amine occurred at temperatures as high as 200°C and that the conditions for rehydration required heat or long exposure to water, it seems probable that the loss of adsorption sites is largely connected with the loss of strongly bound water. In fact, it would appear that hydroxyl groups specifically are involved either directly or indirectly. This view is supported by the greater amine adsorption on surfaces polished with alkaline alumina or alkaline diamond suspension compared with adsorption on surfaces prepared using the neutral diamond slurry. Possibly the metal hydroxide groups are directly involved in that on freshly polished metals they adsorb amine by acting as Bronsted acids and that the decline in adsorption with increasing dehydration temperature is simply due to the condensation of hydroxyl groups to give oxide and water. It is also possible that the sites involved are the metal cations acting as Lewis acids and that these cations become less effective in this capacity because of shortening of the metal-oxygen bond as water is removed from the oxide layer. Such changes in the oxide structure could be the result of the loss of hydroxyl groups or of strongly bonded water not present as hydroxyl groups.

The decline in apparent amine adsorption with increasing pretreatment temperature for the iron, chromium, and nickel substrates parallels the dehydration behavior of the corresponding hydrous oxide gels. Iron and chromium showed a continuous decline in adsorptivity up to about 200°C, whereas the decline in adsorptivity of the nickel occurred in a relatively narrow temperature range between 110 and 120°C. It is known that iron and chromium form hydrous oxide gels which when subjected to isobaric dehydration at the pressure employed here lose water continuously with increasing temperature (15). On the other hand, nickel hydrous oxide gels show a characteristic decomposition temperature of 115°C (16) close to the temperature at which the nickel plates showed their marked loss in ability to adsorb an amine monolayer. In the work that has been reported on dehydration of hydroxide precipitates, the loss of water was essentially complete at 200°C for both chromium and iron (15); this is also the approximate temperature at which the iron and chromium plates studied here reached a minimum in adsorptivity.

It is unlikely that the loss in ability to adsorb the amine at temperatures below 200°C involved further oxidation of the metal surface. However, the regeneration of amine adsorption that took place at temperatures near 200°C and higher clearly did involve oxidation. This conclusion follows from the fact that up to 180°C for iron and 200°C for steel the results were identical whether the surfaces were dehydrated in a current of helium or of air. At pretreatment temperatures above 200°C, amine adsorption was decidedly greater on the test plates heated in air than on those heated in helium. Some assistance can be obtained in interpreting these observations from the large body of work that has been done on the mechanism of metal oxidation (17). For iron and steel it has been shown that at temperatures below 200°C these metals form thin oxide films ranging from 50A to 100A in thickness; at these limiting thicknesses oxidation ceases because the electrostatic potential gradient between the gas/oxide and metal/oxide interfaces is too small to promote further oxide growth. It is probable that thin film formation on the metal substrates would be essentially complete immediately after polishing, oxidation being aided by the fact that the polishing process disturbs a layer at least 100A thick (18).

At temperatures above 200°C the oxidation of iron and steel changes to the mechanism of thermal diffusion of metal cations from the metal/oxide interface toward the gas/oxide interface so that oxidation can proceed continuously. The diffusion of cations into the oxide could explain the regain in amine adsorption at temperatures above 200°C if the oxide formed is richer in metal ion than the oxide film that is formed at lower temperatures.

The temperature at which oxidation of iron and steel by cation diffusion becomes significant is seen to match closely the temperature of 180 to 200°C at which heat treatment begins to produce increased amine adsorption (19). The regain in amine adsorption on nickel and chromium also occurred around 200°C; yet these metals do not begin to oxidize by thermal diffusion at temperatures below 300°C. Since adsorption depends only on the surface layer of atoms and not on the thickness of the oxide film, an alternate and equally plausible explanation of the regain in amine adsorption at pretreatment temperatures above 200°C is that the heating process produces allotropic changes in the microcrystalline structure of the oxide film. Such a reorganization could make more cations available to the adsorbate. The experimental work reported here does not permit a decision as to the relative merit of the two explanations. A similar dilemma has been noted in explaining the regeneration of the adsorption of polar molecules on metal oxide powders from the gas phase (20).

Octadecyl Alcohol and Octadecanoic Acid

The studies with the C₁₈ alcohol and acid indicate that the alcohol is generally incapable of specific interactions with the iron and steel substrates strong enough to permit formation of a close-packed monolayer.

Adsorption of the acid gave less than a close-packed monolayer except when the oxide film was hydrated and the adsorbate solution had been saturated with water, in which case adsorption continued past monolayer formation to the appearance of microcrystals. This effect of water on the behavior of the acid parallels closely the work of Lancaster (4) who found that octadecanoic acid was continuously adsorbed from benzene by wet Fe₂O₃ and Fe₃O₄ powders. Adsorption was limited to a monolayer on the dry powders, but no determination was made of the degree of adsorbate packing. The results here indicate that not only must the oxide be hydrated but the adsorbate solution must also be saturated with water. Evidently, the oxide surface must be maintained in a heavily hydrated condition to permit extensive soap formation. In the experiments on wet iron powders cited it is likely that enough water was trapped by capillarity and carried into the system to saturate the adsorbate solution.

SUMMARY

The adsorption of close-packed monolayers of octadecylamine from hydrocarbon solution onto the polished metal oxide surfaces of iron, chromium, nickel, and stainless steel was found to be a function of the thermal pretreatment of the substrate. Two regimes of behavior were identified: (a) treatment of freshly polished metals in a closed cell at 0.3 to 0.4 mm Hg at temperatures between 25 and 200°C resulted in a more-or-less continuous decline in ability to adsorb a close-packed monolayer of the amine with increasing temperature; (b) heating at temperatures between 200 and 320°C in the low-pressure cell partially restored the ability to adsorb the amine for all of the metals except platinum. Supplementary experiments and the known properties of polished metal surfaces suggested that between ambient temperature and 200°C the decline in amine adsorption is associated with a loss of strongly bound water from the oxide layer. It was not possible to decide whether the loss of adsorption sites was due directly to the removal of hydroxyl groups or to a concomitant shortening of the metal-oxygen bond so

that the cations were less available to the adsorbate. The regeneration in ability to adsorb amine on substrates heated above 200°C was connected with the oxidation of the metal substrate, but it was not clear whether the new adsorption sites were due to cation diffusion to the oxide/gas interface or whether the oxide was undergoing allotropic changes in microcrystalline structure that tended to expose cations.

In anhydrous solution the adsorption of octadecyl alcohol and octadecanoic acid onto iron and steel gave decidedly less than a close-packed monolayer. On the other hand, the acid formed a monolayer and then visible crystallites at the hydrated oxide/hydrocarbon interface when the adsorbate solution was saturated with water. The acid formed less than a close-packed monolayer from wet adsorbate solution when the substrates were first dehydrated at 200 to 280°C.

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Adsorption from solution Metal oxides Dehydration of oxides Polished metal oxides Close-packed monolayer Octadecanoic acid Octadecylamine Octadecyl alcohol						

INSTRUCTIONS

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