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SUMMARY

    The chemistry of tungsten, molybdenum and their oxides are discussed relative to their attack by common reagents in the form of fused salts or aqueous solutions. These are systems which can be used for cleaning and surface preparation during thermo-mechanical processing of the metals or prior to final assembly of parts. Relative attack rates are given. Utility of several systems are compared, including environmental considerations.

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INTRODUCTION

Cleaning of metals during and after metallurgical processing frequently has been viewed as a necessary evil with little attention given to detail With increasing emphasis on material efficiency, surface properties, and environmental ictors, the need for alternate methods and close control has come under increasing scrutiny

Particularly in the case of refractory metals, whose chemical inertness requires the use of highly active reagents, the control and environmental aspects are of paramount importance

Many chemical methods tend to be proprietary and frequently are poorly understood by those who use them Those who encounter the need to process parts ̄ade from refractory metals are hard-pressed to find practical information egarding the chemistry of cleaning or material removal.

Therefore, a review of several chemical systems for tungsten and molybdenum will be presented that should enable the reader to select at least the basic approach to suit his needs.

The emphasis is on materials and methods that can be applied to production processes. Metallographic texts and others such as Reference 1 dealing with surface preparation give recipes for specific metals and alloys. Frequently, however, they involve reagents which are hazardous, unstable, or expensive, and, therefore, unsuitable for large scale or prolonged use

Other techniques are also available such as: mechanical sand-blasting, grinding, wire brushing, and solvent or detergent degreasing and soil removal. An excellent review of some of these has been compiled by Spring ́Reference 2). They will not be discussed here since many are in general use.

CLEANING OBJECTIVES

A cleaning process is designed to deal with one or more of the following: surface scale, general contamination, and removal of base metal.

Depending on process history, the nature of the scale (thickness, adherence, and composition) will vary widely. It can range from a thick oxide layer, with or without residual lubricant (and lube decomposition products), to spotty minor contamination from handling. Also, as shown in Figure 1, parts of the scale may be isolated or nearly so from the exterior surface by mechanical deformation.

Among a host of potential contaminants in wrought products, iron is of primary concern. It can be introduced by contact with steel processing and handling apparatus Others such as aluminum, calcium, carbon, copper, nickel, etc , may also be present as elements but more frequently are present as oxides. They may be deposited on the external surface or embedded in scale or base metal through mechanical deformation or chemical diffusion at high temperature

Removal of a controlled amount of base metal may be desired to

     a   Expose scale and contaminants if they are not contiguous with the external surfaces

     b   Provide a particular surface finish

     c   Achieve a given size (thickness or diameter)

CLEANING OBJECTIVES – contd

These objectives may be sought as a final step following all metal working procedures or applied as an intermediate step to minimize subsequent contamination (prevent further penetration into the base metal).

The following key questions must have definite, specific answers before any system can be evaluated thoroughly or compared with another:

    a. What is clean? Can it be measured?

    b Must base metal be removed? How much?

    c. If only surface scale removal is required, what is its nature?

    d. How fast or how often? What is the volume and rate of material throughput?

For many applications, acceptable appearance in terms of luster or uniformity is sufficient. In other cases, physical and chemical analyses must be used to assure specification compliance.

There are four major systems for cleaning tungsten and molybdenum. These are treated in detail below


MOLTEN SALTS

One of the most common methods of cleaning is to immerse material in molten salt baths, usually operating at 400°C and above. An excellent review of this process is given by Shoemaker and Wood (Reference 3), including many of the chemical reactions involved.

NaOH (M P. 318°C) is the most common base. It's primary reaction with tungsten scale is

$$WO_3 + 2\ NaOH \longrightarrow Na_2WO_4 + H_2O$$

No reaction with the base metal will occur unless oxidizing salts (most commonly nitrites or nitrates) are present. Simplified reactions may be written as:

$$W + 6\ NaNO_2 \longrightarrow Na_2WO_4 + 2\ Na_2O + 6\ NO$$
$$W + 6\ NaNO_3 \longrightarrow Na_2WO_4 + 2\ Na_2O + 6\ NO_2$$
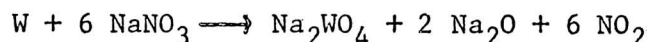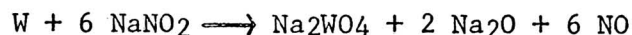
In practice there is much less evolution of nitrogen oxides than predicted from the above equations. The molar ratio of nitrite or nitrate to tungsten consumed is only in the range of 1 to 2. The reaction:

$$2\ NO_2 + 2\ NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O$$
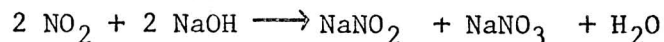
could provide a recycle or regeneration action. The many side reactions of nitrogen compounds, particularly if intermediate oxides of tungsten are involved, can further complicate the mechanism

There are two other oxidizing sources: Air introduced when entering or withdrawing material, and Na_2WO_4 and Na_2CO_3 (see below) themselves are mild oxidizers

At higher temperatures, residual lubricant compounds are oxidized to carbon dioxide This, as well as CO_2 from the atmosphere, results in a gradual build-up of Na_2CO_3 (M P 854°C)

MOLTEN SALTS - contd

As carbonate and tungstate build up, the bath temperature must be increased to retain fluidity Some equilibrium solubility will be reached dependent on temperature with the excess forming an insoluble sludge

Note that contaminants such as iron or its oxide are not chemically attacked by the alkaline media. As the scale and base metal are dissolved, they are physically dislodged forming a finely divided sludge.

The rate of metal attack is proportional to both oxidizer concentration and temperature. For most applications, 1 to 10 weight percent of sodium nitrite or nitrate in NaOH in a temperature range of 350 to 400°C is satisfactory This will give an attack rate of 20 to 40 inches per year for either tungsten or molybdenum. Above 400°C the rate escalates rapidly and at 450°C may be 2 to 5 times greater than the 400°C rate. (The presence of carbonate appears to moderate the rate escalation with temperature.)

If material removal is to be controlled precisely, one must be careful of temperature excursions. Massive pieces in a small volume bath will cool the reaction surface. Large surface to volume ratios may give a "runaway" condition as a result of the exothermic reaction.


AQUEOUS ALKALINE SOLUTIONS

Fully oxidized surfaces (yellow tungsten oxide or white molybdenum oxide) will react with aqueous alkali quite readily, especially if the solution is heated, according to the following: (Except where noted, equivalent reactions may be written for molybdenum)

$$WO_3 + 2 \ NaOH \longrightarrow Na_2WO_4 + H_2O$$
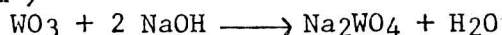
Reduced or intermediate oxides (brown, purple, etc) react slowly if at all. A tightly adherent black scale (with or without carbon) is commonly found on tungsten that has been worked at high temperature. Despite the fact that it is predominately WO_3 (normally yellow in bulk), it is only slowly attacked even by a hot concentrated solution, probably due more to its dense, fused physical state than to its chemical nature.

Five to twenty weight percent solutions give satisfactory action. Temperature and time required depend primarily on the geometry of the work piece and nature of the scale. Higher concentrations seldom are beneficial.

The above solutions will not attack base metal. Like molten salts, they require an oxidizing agent. $K_3Fe(CN)_6$ is a common additive and various formulations with NaOH or KOH are known as "Murikami's etch" in metallographic work

$$W + 4 \ H_2O + 6 \ Fe(CN)_6^{-3} \longrightarrow WO_4^{-2} + 8 \ H^+ + 6 \ Fe(CN)_6^{-4}$$
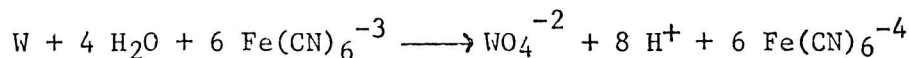
A solution containing 100 grams per liter each of the potassium salt and KOH attack tungsten at about 2 inches per year at 80°C

Another mild oxidizer is hypochlorite.

$$W + H_2O + 3 \ ClO^- \longrightarrow WO_4^{-2} + 3 \ Cl^- + 2 \ H^+$$
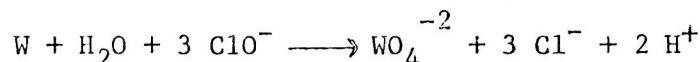
The usual solution of about 5% available chlorine will attack tungsten at a rate of about 3 inches per year at 50°C. Use of this solution is the subject of a patent (Reference 4). However, little information is given on the condi- ns and control of the solution.

The mechanism is much more complex than indicated by the overall reaction in the foregoing equation   This is partly due to thermal or catalytic decomposition:

$$2 \text{ NaOCl} \longrightarrow 2 \text{ NaCl} + O_2$$
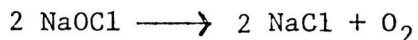
The solution is mildly alkaline via hydrolysis:

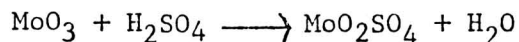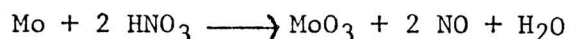$$\text{NaOCl} + H_2O = \text{NaOH} + \text{HOCl}$$
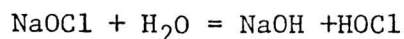
Such oxidizing agents as nitrate and chromate are effective only in <u>acid</u> media   Alkaline permanganate will attack tungsten slowly but is probably undesirable because of the deposition of a black film of manganese dioxide or manganese tungstate.

ACID

Tungsten and molybdenum are much less reactive to individual acids than most common metals   HCl, HF, and H_2SO_4 have essentially no effect. Molybdenum will react rapidly with HNO_3 solutions containing up to about 50 volume percent of the normal reagent (70% by weight). At higher concentrations Mo exhibits a passivity phenomenon similar to iron. Tungsten shows an appreciable reaction with HNO_3 only as fine powder and then heat is usually required.

The most common acid reagent for attacking molybdenum is a <u>mixture</u> of nitric and sulfuric acids.

$$\text{Mo} + 2 \text{ HNO}_3 \longrightarrow \text{MoO}_3 + 2 \text{ NO} + H_2O$$

$$\text{MoO}_3 + H_2SO_4 \longrightarrow \text{MoO}_2SO_4 + H_2O$$

This mixture provides the two requirements for effective base metal attack: an oxidizing agent and a medium in which the oxidation products are soluble. MoO_3 and its hydrates are not particularly soluble in nitric acid but will be complexed in sulfuric acid (expressed as a simple oxysulfate above).

The same mixture has no effect on massive tungsten but may react with very fine powder. However, $HF + HNO_3$ reacts rapidly with tungsten. Tungsten oxides and its hydrates are insoluble in $HNO3$ (as molybdenum above) but in this case are complexed as oxyfluorides

$$W + HF + HNO_3 \longrightarrow H_x WO_y F_z + NO + H_2O$$
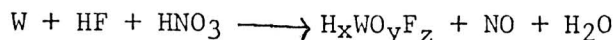
The actual molar ratio of HNO_3 to tungsten is fairly constant at 2 5 to 3 0 but the HF ratio varies considerably. This is probably due to an equili- brium between species such as:

$$H_2WO_3F_2 + 2 \text{ HF} = H_2WO_2F_4 + H_2O$$

ACIDS - contd
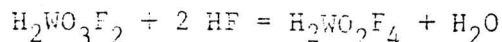
These species are colorless and soluble to the extent of several hundred grams per liter (expressed on a tungsten basis). The same mixture will attack molybdenum even more rapidly.

The only acid solution that will attack tungsten oxide without attacking the base metal is strong HF (48%). Depending on the history of the sample, an oxide scale will exhibit varying degrees of attack by acid systems. In general, acids exhibit a slower and less uniform attack on the scale than the base metal itself.

When tungsten and molybdenum are treated with acid solutions, they frequently are stained by residual oxides - even if rapid and thorough rinsing is used. Especially with molybdenum, it is extremely difficult to avoid a blue and/or brown stain The reason is that as the sample is withdrawn from the solution, the acid continues its attack on the metal:

$$Mo + x\ HNO_3 \longrightarrow MoO_y + x\ NO + 0.5x\ H_2O$$
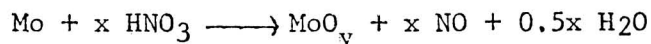
where y is 1.5x. If y is about 2, the stain is brown and almost impossible to rinse off. If y is closer to 3, the stain will be blue and may be water soluble. The acid strength in the liquid film is depleted before total oxidation occurs and the reaction stops at some intermediate point.

This means that oxide generation continues past the point where the sulfuric component can cope with it in terms of solubility. This can be avoided by appropriate selection of acid strengths and rinse conditions.

The use of conventional inhibitors to minimize base metal attack is precluded because of the strong oxidizing conditions.

If a bath of HF-HNO_3 is used to treat both tungsten and molybdenum, the attack on tungsten is more sensitive to HF concentration and the attack on molybdenum is more sensitive to HNO_3 concentration. Also the change in rate with time as the acids are consumed differ for the two metals. All reactions escalate rapidly with an increase in temperature.

To put this in perspective with prior data, a room temperature bath consisting of 174 grams/liter HF and 200 grams/liter HNO_3 (or 30 and 20 volume percent of the usual reagents) will attack tungsten at at rate of about 10 inches per year, and molybdenum at least 5 times faster.
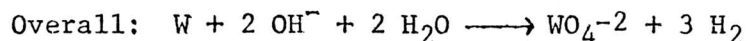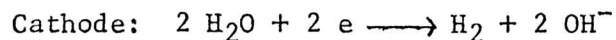
There may be a situation in which the primary surface contamination is iron or some other metallic element from abrasion in handling. If it has not penetrated by diffusion or deformation beyond the accessible exterior surface, a simple dip in dilute hydrochloric acid may suffice.

ELECTROETCH

Electrolytic etching is the removal of base metal by an applied voltage in a medium capable of dissolving the products of the electrolytic reaction This may be done in molten salts or aqueous solutions. It is electrical current and time that determine the amount of metal removed (they provide the same function as the chemical oxidizer in prior sections).

The metal to be cleaned must be the anode where oxidation occurs. The common electrolyte is NaOH where the following reactions occur:

$$\text{Anode:} \quad W + 8\ OH^- \longrightarrow WO_4^{-2} + 4\ H_2O + 6\ e$$

$$\text{Cathode:} \quad 2\ H_2O + 2\ e \longrightarrow H_2 + 2\ OH^-$$

$$\text{Overall:} \quad W + 2\ OH^- + 2\ H_2O \longrightarrow WO_4^{-2} + 3\ H_2$$

The following relationships for metal removal are derived from Faraday's laws:

$$\text{Grams W} = 1.143\ IT$$

$$\text{Grams Mo} = 0.596\ IT$$

where I is current in amperes and T is time in hours.

If AC rather than DC current is used, metal removal will occur only on the anodic half-cycle, doubling the time required for a given amount of weight loss.

The electrolyte may exert some chemical reactivity on surface scale or impurities but this is minimal compared to the current-time effect on base metal attack Therefore, the electrolyte is chosen for its ability to dissolve corrosion products and minimum electrical resistance. For these properties, as well as cost, there are few candidates that can compete with aqueous NaOH.

Electroetching in an acid medium generally is not possible due to the almost instantaneous formation of an insoluble anodic oxide film which insulates against any further action. Exceptions are the use of sulfuric acid for molybdenum and strong hydrofluoric acid for tungsten.

At some point the bath will be depleted as a result of one or more of the following:

    a. Insufficient free NaOH at the anode to provide solubility for the oxidized metal

    b. Electrical resistance too high because of the conversion from NaOH to tungstate or carbonate (from atmospheric CO_2 pick-up)

    c. Build-up of salts beyond solubility limits.

These limiting conditions can be mitigated somewhat by operation at elevated temperatures which will maximize solubility and minimize resistance.

Design of equipment will be based primarily on the geometry and size of the material to be cleaned However, in an effort to minimize time required or maximize throughput, one must be careful to consider the current density involved (amps/unit surface area) Excessive current density can lead to poor efficiency in several ways

    a Polarization effects due to localized depletion of the electrolyte (agitation or circulation will minimize this)

ELECTROETCH – contd

    b   Heat generation from resistance effects causing the electrolyte to boil, thus forming an insulating gas film around the work piece

    c.   Excessive voltage resulting in a competing anode reaction

$$4\ OH^- \longrightarrow O_2 + 2\ H_2O + 4\ e$$
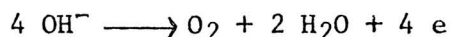
The concentration of NaOH is not critical (5 to 50% solutions have been used). However, it must be recognized that, due to the above reactions, the electrolyte is in a constant state of change, both in terms of chemical composition and electrical resistance.

PROCESS CONSIDERATIONS

General

    A typical sequence is shown schematically in Figure 2. Bath A might be caustic for scale removal and Bath B could be hydrochloric acid for removal of surface iron

    Aside from equipment design and materials handling, a number of factors must be understood before any system can be operated efficiently and with due regard to quality control and compliance with environmental standards. These include the following:

    a   Analytical Control – The reagent consumption rate should be known as a function of the number or weight of parts treated. This permits an estimate of bath life so that make-up or disposal can be scheduled. Analysis of bath composition will confirm this and is particularly important if attack rates are sensitive to concentration changes

    b   Temperature Control – Most chemical reactions escalate rapidly with increased temperature Therefore, cooling and agitation may be required

    c.   Generation of Fumes and Solids (Sludge) – Rate of formation must be known so that they can be handled consistent with production rate and safety standards with minimum interference to material handling

    It may be desirable to utilize the same process and, more specifically if possible, similar concentrations and temperature for more than one material. For example, it might be desirable to compromise conditions for tungsten somewhat in order to treat molybdenum in the same facility to avoid duplication of equipment and services.

    Rinse facilities are last sequentially but their design must be a foremost consideration Erratic or inadequate rinsing may negate whatever benefit was obtained from the cleaning operation itself Furthermore, in terms of disposal and other considerations, it is likely to involve much greater volume than the cleaning system

General - contd

Disposal has become increasingly important since, in most circumstances, dilution and neutralization are no longer sufficient. In the alkaline systems where the metals are present as the simple molybate or tungstate, these may be recovered (and, in fact, have some saleable value) by the addition of a calcium salt to precipitate $CaMoO_4$ or $CaWO_4$ (synthetic powellite or scheelite, respectively). Such recovery may have to be modified depending on the presence and nature of an oxidizer.

The acid systems are more difficult to handle since simple neutralization will still leave both metals soluble as the isopoly species. Precipitation of the calcium salts would be accompanied by large quantities of sulfate and/or fluoride.

System Comparisons

The following is a subjective rating for the main objectives in cleaning along with ease of disposal.

System Rating for Specific Objectives

System	Attack On			Ease of Disposal
	Base Metal (W or Mo)	Iron[a]	Scale[b]	
Molten NaOH	No*	Poor	Good	Good
Molten Oxidizing Salts	Good	Fair[d]	Good	Fair
Aqueous Alkaline Solution	No	No	Fair	Good
Oxidizing Alkaline Solution	Fair	Fair[d]	Fair	Fair
Acid Solution[c]	Good	Good	Poor	Poor
Electroetch (Alkaline)	Good	Fair[d]	Good	Good

a - Used as representative of "tramp" surface metal contaminants.
b - Reactivity varies dependent on physical and chemical nature.
c - Containing nitric acid or other oxidizer.
d - Little chemical attack but may be removed by undercutting base metal.
* - Mo will react above 650°C (this is above the normal salt bath operating temperature).

For rapid attack of heavy scale, molten salt is far superior to the others. Also, if no oxidizer is present, it can be done with no fear of base metal loss.

If appreciable sizes or volumes of material are to be processed, particularly with significant base metal removal, acid solutions present a disposal, if not an operational, problem

System Comparisons - contd

Utility of electroetching is probably more dependent on geometry than the others. For example, it is fine for treating continuous lengths of wire. However, for many small discontinuous pieces there is a contact problem and large pieces may involve a power supply and distribution (uniform current density) problem.

For all systems involving base metal attack, rate control must be achieved by definition of concentration, temperature, and time of exposure.

Rate of Attack

In a manufacturing operation, material removal is commonly monitored in terms of weight loss or dimensional change. For comparison purposes, this is valid only for parts with equivalent geometry and density. More meaningful dimensions are penetration per unit time such as inches per year (ipy), as used in corrosion data. This is determined from weight loss per unit time from a material of known surface and density; i.e.:

$$ipy = \frac{KW}{TdA}$$

If W = weight loss, grams
T = time, hours
d = density, grams per cubic centimeter
A = surface area, square centimeter
Then K = 3.45×10^3

Approximations for these values have been indicated in the text. For tungsten, most systems run from 1 to 10 inches per year with molybdenum being greater by 50% or more.

Greater than 50 mils per year is considered to be a rapid corrosion rate. These reactions discussed here are highly exothemic and the rates are markedly influenced by agitation and geometry of the bath and the work piece.

Therefore, it is far more practical to compare rates for the various solutions in the actual cleaning system rather than perform an idealized "corrosion" test.

More conventional corrosion media are reported in Reference 5.

SUMMARY

With the objective of the cleaning operation clearly defined, one should be able to choose the system or variation thereof that best suits the size and rate requirements. Although the details of reaction mechanisms are not completely understood, enough fundamental chemistry is available to permit composition control and modification of reaction rate. Because of personnel hazards from the reagents and potential environmental impact of a large-scale operation, careful planning and equipment design must accompany the choice of a chemical system

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RJS/bm
10/29/74

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5   W. L. Acherman, et al, "Corrosion Properties of Molybdenum, Tungsten, Vanadium, and Some Vanadium Alloys," Bureau of Mines RI 6715, 1966.
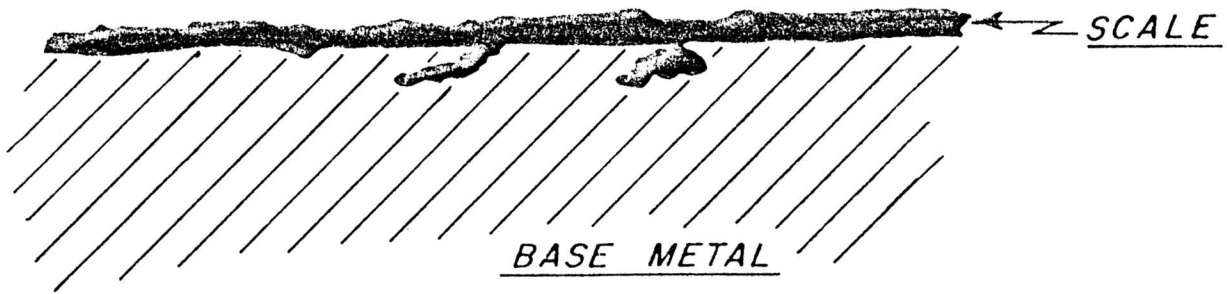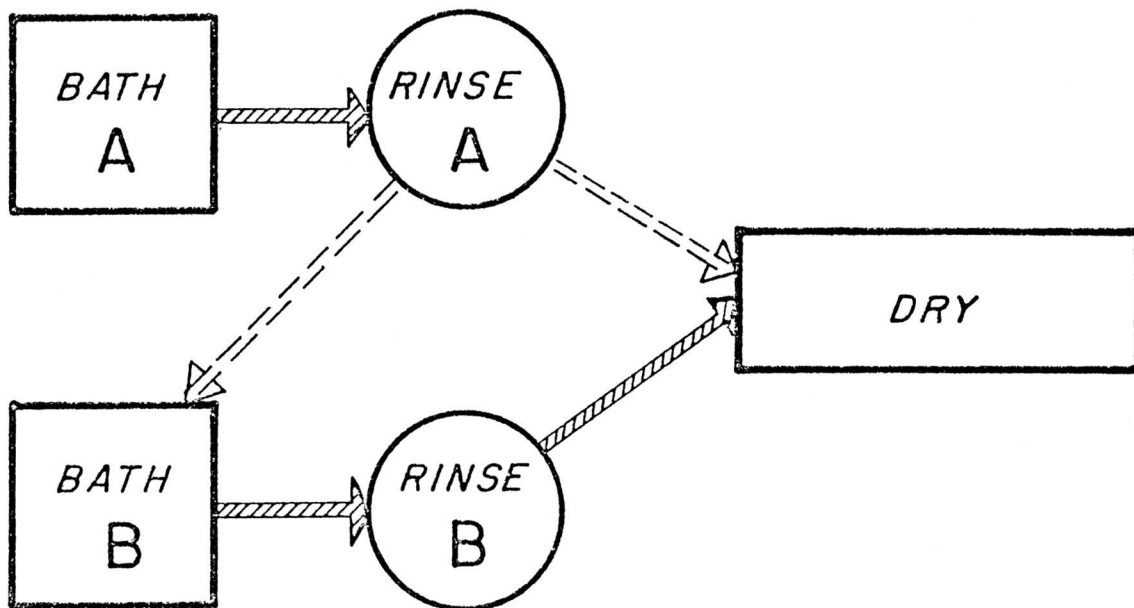
FIG. 1 — SCHEMATIC OF SURFACE FLAWS

FIG. 2 — TYPICAL CLEANING SEQUENCE