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Assessment of Surface Cleanliness for Metal Surfaces using Electrochemical Methods

by

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Thesis submitted in fulfilment of the regulations for the degree of Master of Philosophy at Loughborough University of Technology

July 1994

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Synopsis

Existing methods for qualitative assessment of surface cleanliness are not very accurate. They all show a momentary status of the surface, because measurement during pretreatment is impossible.

Modern high technology methods of manufacture demand assessment methods to describe the effectiveness of a cleaning process very precisely.

Since the phenomena during a electroplating process can be explained in terms of electrochemical reactions, it follows that electrochemical techniques can be used to study interactions between the surface of substrate and the electrodeposited metal.

Electrochemical tests for use on these surfaces have therefore been evaluated. These include potentiodynamic and potentiostatic measurements, polarisation resistance measurement, potential versus time measurement, galvanostatic and impedance measurement on a number of typical samples.

The main object of the examination was to show the principle possibility of a simple, effective and robust two-electrode measurement cell to estimate cleanliness of metals.

To examine the grade of accuracy and detectability of this kind of measurement several electrochemical and other than electrochemical methods were combined.

The literature on the measurement methods and principles of surface cleanliness has been reviewed.

The test methods presented can be applied on a wide range of different production lines for electroplating. These possibilities have been therefore considered in the discussion.
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7. References
1 Introduction

1.1 General Background

Cleaning processes used for removing soils and contaminants on surfaces - especially degreasing processes - are one of the most important steps of surface treatment prior to physical, chemical and electrochemical surface coating processes. In selecting a cleaning procedure to individual application many factors must be considered. Any preferred cleaning conditions must depend on the substrate, the quality and amount of soils and contaminants to be removed and on the degree of cleanliness required.

First of all cleaning processes must be able to generate in a short time a surface of materials free from adsorbed contaminations. They must also be able to generate a surface which has after the cleaning process certain physical and chemical properties for the following process step options: electroplating, phosphating, painting, physical and chemical vapour deposition, corrosion protection, etc.. Cleaning solutions and procedures must be economical (waste water) and compatible with further (chemical) processing. Environmental consideration are also very important. Because of the variety of cleaning materials available and the different kinds of soils and contaminants on the surfaces, several cleaning procedures have been established. Soils and contaminants on metal surface, thus could be unpigmented oil and grease, pigmented drawing compounds, chips and cutting fluids, polishing and buffing compounds, rust (oxide) and scale and different surface contaminants such as lapping compounds and rest of pickling compounds.

Solvent, solvent vapour degrease, emulsion cleaning, alkaline cleaning, electrolytic cleaning, alkaline plus acid cleaning (activation) and finally ultrasonics each progressively produce a cleaner surface by removing these contaminants.

Choice of an optimal cleaning procedure therefore depends substantially upon the type of soil to be removed. In the case of electroplating processes perfect cleaning is very important, since upon the efficiency of cleaning depends the
adhesion and other properties (porosity, structure, etc.) of the deposited metal or alloy. Electrical conductivity can also be critical.

Modern high technology methods of manufacture demand assessment methods to describe the effectiveness of a cleaning process very precisely. But only sensitive and very accurate measuring methods guarantee the correct selection of cleaning processes to ensure that the required standards and the best conditions for further processing have been selected and are maintained.

Several methods of cleanliness measurement exist. Common and well known methods of determining the degree of cleanliness of the metal surface like water-break test, acid copper test, Nielson method, atomizer test, stalagnometer test, conductivity measuring, fluorescent method, wiping method, radioisotope tracer technique and finally the measurement of the weight of residual soil show many disadvantages. Most of these methods are not very accurate and they all show a momentary status of the surface, because measurement during treatment is impossible. Furthermore very few methods of cleanliness measurement are available which can be adapted to production process. In order to be of direct use to the production line a measurement method requires a combination of characteristics. It must be easy to use without specialist competence, reliable enough to give reproducible results and at the same time rapid and cost effective.

Various specialised methods have been developed which make it possible to measure specific contamination on metal surfaces. However a combination of different methods is normally required in order to get a complete picture of the different types of surface contamination e.g. oil residues, oxides and salts. But the biggest disadvantage of these methods is the fact, that solid phase (substrate surface) and liquid phase (cleaning solution) are measured separately - correlations are difficult.

Since the phenomena during a electroplating process can be explained in terms of electrochemical reactions, it follows
that electrochemical techniques can be used to study interactions between the surface of substrate and the electrodeposited metal or alloy. In comparison with decontaminated metal surfaces, contaminated metal surfaces show a very different electrochemical behaviour.

Therefore cleaning processes on the metal surface must have a distinct influence on electrochemical reactions occurring on the substrate surface. Electroanalytical methods, as is well known, provide a sensitive means of detecting species in solution even at low concentrations.

1.2 Project Proposal

This project has been instituted to investigate the possibility for assessing cleaning conditions for metal surfaces using electrochemical methods. It is primarily concerned with the electrochemical polarisation characteristics of metal in different state of cleaning. Some typical kinds of soils and contaminants on various metal surfaces are investigated to show the principle possibility for assessing cleaning solutions by electrochemical methods with the respect to the grade of accuracy and detectability.

In a first step the aim has been to characterise the typical electrochemical behaviour depending to the kind of metal surface, impurities, cleaning solution, cleaning condition and the following process steps. A successfully tested possibility is the principle of the potentiodynamic three electrode measurement in a alkaline solution containing $10 \text{ g/l KOH}$. Different impurities and different cleaning conditions causes different mechanism on the electrochemical reactions (causes different curves) and therefore on the quality of the deposited layer.

For example organic compounds cause a decrease of the anodic current because of their low conductivity. Organic compounds are oxidised on silver, copper, copper alloys and steel electrodes in a potential range where electrodeposition of metals not occur (+0.4 to +0.8 V versus hydrogen electrode NHE).
Impurities like oils from drawing on copper and copper alloys cause a typical electrochemical "finger print". For example this fingerprint allows one to find out the best cleaning conditions for brass and bronze due to following tin deposition. Copper oxides cause a low anodic current and a degrease of the current maxima of the potential/current density curves.

In the second step of investigation the "typical range" of current (current density) was used to continue with two-electrode measurement. This is based on two circuits that are wholly independent of one another. The first is the current circuit, which connects working electrode and counter electrode to a constant current source. The second circuit, the measurement circuit, connects working and reference electrodes to a potential measurement device. Using very low currents (< 10 µA) a potential measurement device with high impedance is necessary to prevent errors as the current in the measurement circuit forms a significant part of the total current.

A detailed investigation of the factors affecting the results from this method has been made. In detail organic compounds on noble (gold, silver) and semi-noble metals (copper, copper alloys), oxides and unpigmental oil on copper alloys (brass, bronze) and pigmented drawing compounds on steel surfaces were investigated. Various cleaning conditions e.g. solvent, alkaline cleaning with and without ultrasonics, electrolytic cleaning and pickling are used.

Additionally for comparison different analyses of different metal surface and different tests under production conditions of the system substrate/upper layer (metallic or non-metallic) have also been made.

From these experiences, and after optimising the measurement conditions (electrode, cell, current, solution, time, temperature, etc.), this technique could be a very quick, cheap and sensitive method to characterise impurities on metal surfaces, cleaning solutions, cleaning conditions and their influence on following surface treatment processes. It could
also be the basis for an assessment method that could be used to optimise process efficiency. Therefore this project attempts to show the principles to be studied in further projects, in order to develop a quality control technique for monitoring process cleaning as a pretreatment step for surface coatings.
2. Review of Literature

In earlier times cleanliness of metal surface was not considered to be an important step of pretreatment in surface coating processes. In selecting a cleaning procedure visual judgement was normally the only quality control to satisfy requirements on clean surface. For example, in the past the influence of substrate surface condition to porosity of electroplated layers was not so important because of much higher thicknesses of the electroplated layers. Definite properties of the coatings were not necessary because most of the application was for decorative use than for functional use.

Nowadays application of physical, chemical and electrochemical surface coatings is different from this [1,2,3]. For example in ninety-nine times out of a hundred electroplated layers are desirable with special properties. Therefore, the electroplating technique changed from an empirical and artistic craft to an high technology [4,5,6]. Electroplating is used as an surface treatment technology which can create definite surface properties. Single metal and metal alloy coatings with special structures, chemical and physical behaviour are required [2,7,8]. Because of manufacturing costs and smaller size of workpiece thickness of the electroplated layers decrease. In the case of nano-layer deposition the influence of the substrate surface increase and become more important for all properties of the coatings [9,10,11].

From such considerations cleanliness of a substrate surface has become more important [12,13]. Pretreatment and specially cleaning processes must fit in with the whole surface treatment processes (pretreatment, coating and posttreatment) [14-18]. Complete quality control programmes [19-27], essential for maintaining both the excellence of performance and the durability required of modern manufactured products, require the most effective cleaning systems available [28-34].

In contrast, cleaning procedures are subject to changes because of the continuous evolution of new and faster production techniques with lower cost of manufacturing, new chemical solutions and machines and very strict environmental laws at present [35-42].
In the selection of a metal cleaning process many factors must be considered including [18,43-45]:

- Identification and characterisation of the substrate to be cleaned like shape and size, condition of the surface structure to the ultimate use
- Identification and characterisation of the soil to be removed
- Subsequent operations to be applied
- Degree of cleanliness required
- Constituents of the cleaning solution
- Cleaning conditions
- Impact of the process on the environment
- Capabilities of the process on the environment
- Overall cost of the process

2.1 Task of Cleaning Process

Cleaning processes should prepare the surface of metals for the following coating process or other chemical processes. Cleaning process must therefore remove [46-51]:

- Particles from air and dust, particles from grinding, honing and particles from lapping compounds
- Impurities which prevent wetting of the surface like silicone, grease and oils
- Impurities which degrease the ultimate behaviour like salts and other chemical inorganic compounds
- Electrochemical reactivity of the metal surface for further coating processes
- Metal surface must be immune against corrosion during the cleaning procedure and also during following treatment operations like rinsing and drying during storage
2.2 Types of Soil on Metal Surfaces

In the context of cleanliness it is expedient to create a classification according to the solubility of soil. For this soil can be generally divided into three main areas [16,18,37]:

- Soil soluble in organic solvents
- Soil soluble in aqueous chemical solutions
- Mixed soil containing particles

Table I  Types of Soil on Metal Surfaces

<table>
<thead>
<tr>
<th>Soil on Metal Surface</th>
<th>Organic Soil</th>
<th>Inorganic Soil</th>
<th>Mixed Soil with Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble in Organic Solvent</td>
<td>Soluble in Aqueous Chemical Solution pH 4-14</td>
<td>Insoluble in Aqueous Chemical Solution pH 4-14</td>
<td>Low Adhesion Removable in Solvent and Aqueous Solution</td>
</tr>
<tr>
<td>Melting Point &lt; 100°C</td>
<td>Saponification or Solubilisation possible in Aqueous Chemical Solution</td>
<td>Soluble in Solution Containing Complexing Agents pH 4-14</td>
<td>High Adhesion Removable in Special Aqueous Solutions</td>
</tr>
<tr>
<td>Melting Point &gt; 100°C</td>
<td>Difficult to Remove in Aqueous Chemical Solution</td>
<td>Soluble in Aqueous Chemical Solution pH 4-14</td>
<td>Very High Adhesion Removable only with Support of Mechanical Treatment or Dissolution of the Substrate</td>
</tr>
<tr>
<td></td>
<td>Soluble in Acid Solution pH &lt; 4</td>
<td>Soluble in Acid Solution pH &lt; 4</td>
<td>Insoluble in Acid Solution pH &lt; 4</td>
</tr>
</tbody>
</table>
2.2.1 Organic Soil

Organic soils consist of mineral, animal and vegetable substances like oil and grease of various types, waxes and different organic materials. Organic or mineral soils are not commonly encountered in the pure state since most commercial mineral oils are employed in the compounded state. In the case of grease and oil as well as in the case of contaminants like metal particles, dust, lapping and buffing compounds bonding mechanism is a physical bond. But in contrast to these compounds grease and oils are easy to remove because they are soluble in alkaline or solvent cleaners. Therefore they can be removed by appropriate organic solvents either by dipping the workpieces in the solvent or, more regularly and effective, by vapour degreasing.

2.2.2 Inorganic Soil

Inorganic soils include rust, smut, tarnish, solid dirt, dust scale and various residues resulting from pickling, cleaning or some other pretreatment processes. Pickling residues are carbide or graphitic material (very difficult to remove) often mixed with different types of organic inhibitors used to control the pickling action in acid solutions. Residues from prior cleaning processes are mostly metallic soaps formed during saponification process. Inorganic soils are normally insoluble in solvent solutions and therefore generally very difficult to remove. Solubility depends primarily on pH of cleaning solution and content of complexing agents. They are usually removed by alkaline cleaning, with and without ultrasonic agitation and/or electrolytic cleaning. Rust and tarnish are insoluble in water but can be removed either in acidic solutions or by alkaline chelating solutions. Insoluble solid particles often adhere to the oil on the surface and are therefore removed along with the oil. A type of inorganic soil which causes a lot of trouble may be oxide films or films of phosphate, silicates and the like which remain on the surface after prior alkaline cleaning. They are very hard to remove both by rinses as by acid dips. To eliminate this sort of trouble carefully rinsing with water of high purity is the preferred way.
2.2.3 Mixed Soil

These types of soil are sometimes troublesome to remove since they are composed of animal, vegetable and other oils and greases with abrasive metal particles or other large and small particle debris mixed with lubricants left by machining, grinding or polishing operations and other e.g. buffing compounds residues (pigmented drawing oils, carbonised oil deposits) [3,18]. Furthermore on the surface of the substrate could be films of oxides, phosphates, silicates, other inhibitor films and passive layers [12,13]. Gases such as hydrogen, may also be adsorbed on or in metals e.g. in the cathodic cleaning of steel [53-55].

Some particles like particles from grinding and honing are easy, some particles like lapping compounds are hard and some particles like MoS2-pigments are very hard to remove from metal surfaces [56,57]. To remove such particles with strong adhesion to metal surface cleaning procedure must be support by abrasive brushing, wiping, water jet beam, turbulent floating, anodic or cathodic electrolytical degreasing and/or ultrasonic agitation [16-18,46,50,58].

In table II typical types of soil on metal surfaces and possibilities to remove is shown [59]. It is noticeable that in special cases some different possibilities are useful because of influence of several factors, like:

- Change of surface depending on amount and thickness of soil
- Change of surface during storage and heat treatment
- Change of surface by chemical reaction

In general organic soil is highly soluble in solvent cleaners. In case of cleaning in aqueous chemical cleaners, melting point or dripping point of soil is important for their solubility. Inorganic soil normally is not soluble in solvent cleaners. Their solubility is definite by pH of the cleaning solution and the amount of complexing agents.
### Table II: Types of Soil on Metal Surface and the Possibility of their Removal

<table>
<thead>
<tr>
<th>Type of Soil</th>
<th>Solvent Cleaners</th>
<th>Aqueous Chemical Cleaners</th>
<th>Mechanical Support</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acid Cleaners (phosphate)</td>
<td>Neutral Cleaners</td>
<td>Alkaline Cleaners</td>
</tr>
<tr>
<td>rust (filmrust)</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>oxides (Al)</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>tarnish colour</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>abrasion (metal particles)</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>dust</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>phosphates</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>soaps</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>oxalates</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>chromate layers</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>inorganic passiv. compounds</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>organic passiv. compounds</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>oils for corr. protection</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>waxes for corr. protection</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>soldering compounds</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>fluxes</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>oils emulsifiable</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>oils not emulsifiable</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>soaps (reactive)</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>grease/soaps mixtures</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>pigments soluble in water</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>pigments not soluble in water</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>finger sweat</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>petroleum</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>C-pigments</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>MoS₂-pigments</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>lapping compounds</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
<tr>
<td>grinding compounds</td>
<td>♦</td>
<td>♦</td>
<td>♦</td>
</tr>
</tbody>
</table>
2.3 Theory of Cleaning

In order to clean a metal surface, it must be assumed that soil is adhering to it. If no bond exist between the substrate and contamination, then it must be assumed that the dirt will fall off or it can be blown or floated off. This type of soil does not present a serious problem. But normally several bonding mechanism exist between a metal surface and the contaminating soil. Physical bonds like physical absorption and chemical bonds like valence and adsorption (chemisorption) bond are formed.

In most cases there is more than one bonding mechanism present, but in all cases if cleanliness is required it is necessary to eliminate or destroy the bond by several kind of energy.

Therefore, the first requirement for cleaning is that energy must be applied at the point where the bond between soil and metal surface has to be broken [58-60]. By energy, a combination of mechanical (agitation, ultrasonics and spraying), physical (temperature, surface tension, etc.) and chemical (polar attraction, etc.) energies can be added together. The higher the energy the more efficient the cleaning [61,62].

A Cleaning process as a preatreatment in electroplating steps involves the action of certain chemicals [63], which lifts the soil from the surface of the workpiece or tend to displace it so that it can be flushed away by either the cleaner or a water rinse [62]. The speed and efficiency with this takes place are dependent upon e.g. heat and the level of agitation. Agitation is for more significant when soils contain finally divided particles or are viscous. Cleaning is accomplished by one or more of the four major mechanisms:

- Dissolution
- Saponification
- Emulsification
- Dispersion
The four mechanisms can operate independently or in combination which each other. Dissolution is during electroplating process the most usual one for cleaning metal surfaces. Saponification mechanism is limited to soil which will chemically react with alkaline salts in the cleaning solution. Emulsification and dispersion mechanisms are effective on almost any liquid organic soil that is insoluble in water.

2.3.1 Saponification
Saponification means the hydrolysis of an ester to a soap by a caustic alkali, with glycerol as a by-product. Fatty compounds, both animal and vegetable, are saponified by the alkaline salts in an alkaline cleaner that can be converted into water-soluble soaps. Widely used e.g. in electronics industry to render rosin flux residues water-soluble by reacting them with aqueous solutions of organic amines [16].

2.3.1 Emulsification
Emulsification joins together two mutually insoluble liquids such as oil and water. Generally, emulsification requires either a violent mechanical action or an emulsification agent, properly called a surface active agent or surfactant to form or to remain stable. Such surfactants have a water soluble chemical grouping on one end and an oil soluble chemical grouping on the other end [62,63].

In a cleaning solution the water soluble end of the detergent has been solubilised in the water with the oil soluble end still needing a media where it will be soluble. Upon encountering the oil on a part, the oil soluble end is immediately solubilised, and because there is more water than oil, the water phase completely surrounds the oil. Environmental limitations minimise the use of emulsifiers.

2.3.3 Dispersion
In dispersion, the surfactant acts to lower the surface tension of the cleaner at the metal surface, allowing the cleaner to cover the metal uniformly. The interfacial tension of the cleaner is lowered, permitting the cleaner to penetrate the oil film and break it into smaller units. The oil is dis-
persed into small droplets, which are undercut by the film of cleaner spreading across the metal surface. These droplets lose their attraction to the metal and float to the cleaner surface where they reassemble into a semi-continuous film.

2.4 Removal of Soil

2.4.1 Pretreatment Steps

Pretreatment is the preparation of a surface usually in several steps for following coating processes. Because of different types of contaminations and different types of coating procedures, pretreatment must be divided into two stages:

- Preliminary pretreatment
- Final pretreatment

2.4.2 Preliminary Treatment

The main task of preliminary pretreatment is the removing of heavy surface soils, such as grease, buffing compound, drawing compound, scale, heavy rust and burnt oils. This technique involves one or both of two basic treatment steps:

- Removal of heavy amounts of oil, grease, buffing compound, drawing compound, etc.
- Removal of scale, heavy rust, burnt-in oil, etc.

These steps are only followed when required, as determined by the kind and degree of contamination. The methods for accomplishing the first step may in most cases be used for all basis metals. Solvent cleaning and emulsion cleaning are typical [17,36].

The methods for accomplishing the second step vary depending on the type and design of metal substrate and the type of following electroplating processes. Acid dipping and salt bath treatment are typical.

2.4.3 Final Treatment

In comparison the final pretreatment removes only the last traces of oil and grease and conditions the surface for fol-
lowing electroplating. Alkaline cleaning with and without electrolytic support (anodic or cathodic or both reversed) are typical. Additional acid dips in this final stage do not remove scale or heavy rust from the surface of a metal. They are only to neutralise the last traces if alkaline cleaner remaining after rinsing and to activate the surface for the electroplating step. In practice, where both, oil and oxide contamination, could be on the surface, it is a better way to remove the greasy material before attempting to remove rust or scale unless the oxide scale is to be removed by mechanical means.

The amount of soil on a metal surface depends on viscosity of the soil and roughness of the surface. Therefore different types of energy is required. The kind of cleaning procedures can be divided in four broad categories:

- Immersion cleaning
- Spray cleaning
- Electrolytic cleaning
- Ultrasonic cleaning

Immersion cleaning is used for large and single workpieces in baskets and rotating barrels. Normally it is a pretreatment step before decreasing procedure. Cleanliness increase when immersion cleaning is enhanced by pumping and cathodic agitation.

Spray cleaning is a very intensive kind of cleaning procedure and is used when numerous workpieces have to be cleaned.

Electrolytic cleaning is mostly used as a final pretreatment step (after alkaline immersion cleaning) when electrochemical coating follows. Cleaning efficiency is enhanced by hydrogen and oxygen generation.

Ultrasonic cleaning especially is used in electronic, electrical and optical industry when parts with a very high degree of cleanliness are required.
2.5 Types of Cleaners

During cleaning processes different possibilities of physical, chemical or physico-chemical nature come into action. While vacuum and mechanical procedures are physical methods, solvent and emulsion cleaning are physico-chemical procedures, used for soils like oil, waxes, grease, lapping and grinding compounds. Chemical and electrochemical methods are cleaning procedures in acid, neutral or alkaline aqueous solutions or salt bath treatment. In the case of electroplating following cleaners are of importance:

- Organic solvent cleaners
- Emulsion cleaners (semi-aqueous cleaners)
- Aqueous cleaners

2.5.1 Organic Solvent Cleaners

Solvent cleaning is a surface pretreatment process, which has stood the test of time for removing organic compounds such as grease or oil from the surface of a metal. Organic compounds are easily solubilised by solvent and then removed from the workpieces. Furthermore solvent cleaning before other surface preparations can extend the life of cleaning solutions and therefore it reduce pretreatment costs. On the other hand solvent cleaning prepares workpieces for the next operation, such as painting, further machining or packaging. But, because of the serious damage to the environment [64,65], solvent cleaning at present is only allowed in closed equipment [66-68] and in the near future a replacement by other techniques [69-72] could be expected; therefore this technique in plating shops decrease and will be of less importance in the future. In case of electroplating, solvent cleaning is usually followed by an alkaline washing or other similar processes which provide an oil-free surface.

Solvent cleaning of metal surface can be divided into two categories:

- Vapour degreasing
- Cold cleaning
Solvent cleaning solutions can operate at room temperature or by using vapour degreasing techniques. Some authors divide cold solvent cleaning in warm temperatures (treatment below boiling point of the solvent) and cold cleaning [73-75]. But both room temperature solvent cleaning, which covers diverse cleaning of metal surfaces with solvent or solvent mixtures at or near room temperatures and solvent cleaning at temperatures between 25-50 °C, is referred to as cold cleaning by most of the literature.

Cold solvent cleaning is a main treatment process for removing oil, grease, loose metal chips, and other contaminants from the surfaces of metals. Common organic solvents such as aliphatic petroleums, chlorinated hydrocarbons, chlorofluoro-carbons, or combinations of these classes of solvents are used.

Workpieces are cleaned by being immersed in the solvent, with or without agitation. Workpieces that are too large to be immersed could be sprayed or wiped with the solvent. Ultrasonic support is sometimes used in conjunction with solvent cleaning to loosen and remove soils, such as abrasive compounds, from deep recesses or other difficult to reach areas. Using ultrasonics during degreasing procedure, reduces the exposure time required.

Vapour degreasing is the process of solvent cleaning parts by condensing solvent vapours of a non-flammable solvent at its boiling point on workpieces. It needs a specifically designed equipment. Procedure uses the hot vapours of a chlorinated or fluorinated solvent to remove soils, particularly oils, greases and waxes, because of their very aggressive action on such substances. Only halogenated solvents like trichlorethylene (C\(_2\)HCl\(_3\)), perchlorethylene (C\(_2\)Cl\(_4\)), trichlorethane (C\(_2\)H\(_3\)Cl\(_3\)), methylenechloride (CH\(_2\)Cl\(_2\)) and trichlorotrifluoroethane (C\(_2\)Cl\(_3\)F\(_3\)) are used in vapour degreasing. Additionally chlorinated solvents are stabilised or inhibited to resist the harmful effects of some contaminants like sulphur, chlorine or a high content of free fatty acid.
The solvent is heated to boiling in a suitable tank to produce solvent vapour. The temperature differential between the hot vapour and the cool workpiece causes the vapour to condense on the cool surface, dissolve the soil and remove it from the metal surface by dripping back into the boiling solvent. Under certain circumstances, it could happen that hot vapour may bake on some soils and make them difficult to remove, but in generally vapour degreasing is an improvement over cold solvent cleaning, because the parts are always washed with pure solvent.

For impurities which are insoluble in solvent and therefore hard to remove, like inorganic particles with strong adhesion to metal surface, cleaning efficiency in the liquid phase of a vapour degreasing cycle can be considerably increased by the application of ultrasonic energy equivalent to cold solvent. But because of the higher manufacturing costs this procedure is hardly used and limited to some special applications like the removal of soldering flux from printed circuit boards [16].

2.5.2 Emulsion Cleaners (Semi-Aqueous Cleaners)

Emulsion cleaning is mainly used for workpieces of large design or in the case when corrosion resistance is required. Because emulsion cleaning does not generate a water-break-free surface, for electroplating processes this technique is unusable as a single cleaning treatment. Therefore, it is usually followed by an alkaline cleaning system to completely remove the last traces of contaminants or residues of solvent. The process uses organic solvents dispersed in an aqueous medium aided by an emulsifying agent (semi-aqueous cleaner) to remove soil [16-18, 46]. Depending on the solvent used, cleaning is done at temperatures from room temperature to nearly boiling point of solvent 80° C.

An emulsion system contains two mutually insoluble or nearly in-soluble phases. One of which is dispersed in the other in the form of globules. One phase is usually a hydrocarbon and the other is water. The dispersed phase is a continuous phase
and distributed as globules in the liquid. Because oil and water do not mix, an oil-in-water dispersion that does not contain an emulsifying agent, or dispersant, requires constant mechanical agitation to prevent the oil and water from separating into two layers.

Emulsifying agents can be placed in two categories:

- Agents that promote the formation of solvent-in-water emulsions with water constituting the continuous phase
- Agents that form water-in-solvent emulsions, in which water is the dispersed phase.

Furthermore, emulsion cleaners can also be classified into four groups based on stability. Stable, unstable, dispersive, and other emulsion cleaners cover a wide range of solvent and emulsifier compositions. The solvent is generally of petroleum origin and may be heterocyclic.

Because the solubility factor increases as the molecular weight of the solvent approaches that of water, low-to-medium molecular weight solvents are usually more effective in removing soils; however, fire hazards and evaporation losses increase as boiling and flash points decrease.

Emulsifiers include:

- Non-ionic polyethers and high molecular weight sodium Amine soaps of hydrocarbon sulfonates
- Amine salts of alkyl-aryl-sulfonates (anionic)
- Greasy acid esters of polyglycerides
- Glycerols
- Polyalcohols
- Cationic ethoxylated long-chain amines and their salts

Emulsifiers must have some solubility in the solvent phase. When solubility is low, it can be increased by adding a coupling agent (hydrotrope), such as a higher molecular weight alcohol, ester or ether. These additives are soluble in oil and water.
Stable single phase, or permanent emulsion is one in which the discontinuous phase is dispersed throughout the continuous phase. This requires no more agitation to maintain a uniform dispersion than that provided by thermal gradients and the motion of the work being cleaned.

An unstable single phase emulsion has a uniformly dispersed phase that tends to separate and form a solvent layer. Solvents with specific gravity of less than 1.0 g/cm$^{-3}$ form a top layer and those with a specific gravity greater than 1.0 g/cm$^{-3}$ form a bottom layer. These cleaners require moderate to considerable agitation to maintain complete dispersion.

A diphase, multiphase, or floating layer emulsion cleaner forms two layers and can be used in this separated condition. Workpieces are immersed through the solvent-rich surface layer into the water-rich lower layer, permitting both cleaning phases to come in contact with the surfaces to be cleaned. When used in a spray system, a diphase cleaner resembles an unstable single phase cleaner, because the solvent and water phases are mixed in the pumping action.

An emulsifiable solvent system is one in which the as received, undiluted solvent is applied to the surface to be cleaned by hand or by use of a dip tank and is followed by a water rinse that emulsifies and removes the solvent and soil.

Factors that influence the selection of stable, unstable or diphase emulsion systems include:

- Type of soil to be removed
- Size and quantity of workpieces
- Need for corrosion protection
- Water condition
- Cleaning sequence (especially if emulsion cleaning is preceded by alkaline cleaning)
- Cost
Stable Emulsion Cleaners
Stable emulsion cleaners are the most economical of the three emulsion cleaners. They contain hydrocarbon solvents such as kerosene, which can dissolve and clean light shop soils (e.g. in-plant rust protection). Such a cleaner maintains an emulsion with water for many hours, requiring a minimum amount of agitation. But stable emulsion cleaners do have disadvantages. Their efficiency is low in removing hydrocarbon soils at a certain amount and by using under production conditions hard water, stable emulsions can form insoluble precipitates that may plug drains and increase maintenance.

Unstable Emulsion Cleaners
Unstable emulsion cleaners, although higher in cost than stable emulsions, perform more efficiently in removing heavy shop soils, such as oil-based rust preventives and lubricants used in stamping and extruding. The hydrocarbon fraction of unstable emulsion cleaners makes more intimate contact with the surface, permitting greater action of the solvent on soil. Unstable emulsions are also successful in hard waters that cause stable emulsions to break down. However, the cleaning power of these emulsions approaches that of diphase systems and they are widely used for the removal of heavy hydrocarbon soils. Phosphates may be added to hard waters to increase the efficiency of unstable emulsions. When cleaning in unstable emulsions follows alkaline cleaning, the alkali carry over forms soap and causes excessive foaming. Therefore, stable emulsion cleaners are preferred when these cleaning methods are used in sequence.

Diphase Emulsion Cleaners
Diphase emulsion cleaners are used for removing the most difficult hydrocarbon soils, such as lapping compounds, buffing compounds, and oxidised oils. They can provide a higher degree of cleanliness than can be obtained with stable or unstable emulsions. The flash points of diphase emulsion cleaners cover a wide range, permitting operating temperatures up to 80 °C. The monomolecular layer of oil that remains after diphase cleaning provides good rust protection. In diphase cleaning, the solvent in the bottom phase is very powerful and a 100% concentrated product.
2.5.3 Aqueous Cleaners

Aqueous solutions for metal cleaning can be alkaline, neutral or acid solutions. In any case the active substances are specific surfactants. They typically have a water soluble chemical grouping (hydrophile) on one end and a solvent soluble grouping (hydrophobic) on the other end. Therefore they concentrate on the interface and are able to replace others molecules there. Following the charging of the surfactants a distinction is possible: surfactants can be anionic, cationic, non-ionic or amphoteric. Amphoteric surfactants are both anionic and cationic, depending to the pH of the solution. They become anionic in alkaline solutions and cationic in an acid media. Surfactants can be high-foaming, low-foaming or non-foaming and the proper selection is important in electrolytic and spray cleaning. According to pH and typical composition of the solution aqueous cleaners can be divided in:

- Acid Cleaners pH: 4.5 - 6
- Neutral Cleaners pH: 7.5 < pH < 10
- Alkaline Cleaners pH: > 10

2.5.3.1 Acid Cleaners

Acid cleaners are solutions in which a solution of mineral acid, organic acid, or acid salt, in combination with wetting agents, inhibitors, solvents and other detergents is used to remove smaller degree of soil. These type of cleaner has the limitation of not removing oils and drawing compounds. However, acid cleaners are excellent in removing scale and rust, such as the rust formed during storage on steel surfaces. Acid cleaners with alkaline hydrogen phosphates (builder) act as corrosion inhibitors by forming thin passive films (oxides and phosphates) on iron and steel surface.

Treatment can be done with or without the application of heat. The distinction between acid cleaning and acid pickling is the matter of degree. Acid cleaners are more dilute than acid pickling solutions. This cleaning procedure suitable prepares parts for painting, but for parts to be electroplated the acid cleaning cycle usually is followed by alkaline electrolytic cleaning.
2.5.3.2 Neutral Cleaners

Neutral cleaners do not contain any typical in-organic substances (builder), like silicates, carbonates, phosphates, borates and alkaline salts. Cleaning effect is mainly caused by the combination of different organic surfactants and inhibitors. An advantage of neutral cleaners is the fact, that all components are liquid; Crystallisation of components after cleaning process does not occur. Furthermore, cleaning of metals sensitive to alkalis (zinc) is possible, because of lower pH (pH 7.5 - 10) of the cleaning solution. A disadvantage of neutral cleaners is the lower degree of cleanliness obtainable.

2.5.3.3 Alkaline Cleaners

Alkaline cleaners are the most common cleaners used to remove soils from the surface of metals when electroplating processes follows. Soils removed through alkaline cleaning include: oil, grease, waxy solids, metallic particles, dust, carbon particles or silicates. Alkaline cleaning is applied by immersion, spray or electrolytic cleaning. The metal surface is cleaned by dissolution, emulsification, dispersion, saponification or combinations of these mechanisms. The cleaning step is usually followed by a water rinse and then a conversion coating or electroplating.

☐ Method of Application

- Immersion Cleaning

The workpiece to be cleaned is placed in the alkaline cleaning solution, which allows the cleaning solution to come in contact with their surface. After the alkaline cleaner has affected the soil on the metal surface, the soil is removed from the surface by convection currents in the solution which are created by heating units or through some mechanical means of solution movement (ultrasonic and agitation).

- Spray Cleaning

Spray cleaning is accomplished by pumping the cleaning solution from a reservoir through a large pipe, or header, to a series of smaller pipes off the header, called risers, and
finally out of spray nozzles on the riser onto the part to be cleaned. In general, the higher the spray pressure, the more mechanical help is provided in removing soil from the metal surface. This is especially true with small electrically charged particles such as dust, carbon smut, and silicates. Spray cleaners are prepared with low foaming detergents which are not usually as effective as those found in immersion cleaners.

- Electrolytic Cleaning
Electrolytic cleaning is a specialised form of alkaline cleaning in which electrodes are placed in a cleaning solution. Direct current is passed through the solution, and the workpiece to be cleaned is made either the anode or the cathode. Cleaning effectiveness is enhanced by the scrubbing action of oxygen (anodic) or hydrogen (cathodic) gas which evolves at the electrode: Choice may depend on side reactions of metal oxidation or hydrogen adsorption.

- Components of Alkaline Cleaner
Components in a good alkaline cleaner must be readily soluble in water and their solutions must possess superior ability:

- wet the surface of the metal being cleaned
- wet and penetrate the soil being removed
- dissolve or saponify animal and vegetable oils and grease
- emulsify and suspend the insoluble (or unsaponifiable) oils and metal particles
- soften water and rinse freely
- prevent insoluble time soaps
- prevent attack on metal surface
- neutralize acid substances
- high degree of cleanliness
- high efficiency (short treating times)
- average equipment
Some special electrolytic cleaners are known as derusters. Derusters are more effective than standard cleaners and often contain chemical complexants. They are normally used with periodic reverse cycles, in which both anodic and cathodic cleaning are used in the operation, as well as for non electrolytic immersion cleaning. While used with periodic reverse, these cleaners remove a small amount of metal from the workpiece being cleaned, leaving the part with an active, clean surface. The cycle must end with the workpiece as the anode to prevent a layer of unbonded metal from being deposited on the workpiece.

Alkaline cleaners are comprised primarily of three major types of components:

- **Builders**
- **Additives (Organic or Inorganic)**
- **Surfactants**

**- Builders**

Builders are the alkaline salts in an alkaline cleaner. They are usually a blend selected from the following groups: alkali metal orthophosphates, alkali metal condensed phosphates, alkali metal hydroxides, alkali metal silicates, alkali metal carbonates, alkali metal bicarbonates, and alkali metal borates. A blend of two or more of these builders is used for cleaning performance, physical properties of the dry blend, and economics.

The alkali metal is usually sodium. Because of the blend of builders used, some alkaline cleaners do not have any free alkalinity, and they must be controlled by total alkalinity titrations.

These cleaners are usually specialized and the pH of the cleaner solution is intentionally maintained under pH = 9 to maintain stability of one or more of the cleaners components, keep the cleaner from attacking the metal substrate, or for some other special purpose.
- Phosphates

Phosphates serve a multiple function in the cleaner. They act to soften the water, eliminating the flocculent precipitate caused by calcium, magnesium, and iron. They act as a soil dispersant, a source of alkalinity, and as a buffer, which prevents large changes in the level of alkalinity. Some common phosphates used are trisodium phosphate, disodium phosphate, tetrasodium pyrophosphate, and sodium tripolyphosphate. Phosphates also do not corrode unnoble metals. Like emulsifiers, phosphates are subject to environmental regulations which limit the amount of phosphorus allowed in discharged water.

- Silicates

Silicates are also multifunctional. They provide alkalinity, keep soil suspended (especially pigments), provide some detergency and act as an inhibitor, protecting metals such as aluminium and zinc from attack by other alkaline salts. Commonly used silicates include sodium silicate and sodium disilicate.

Silicates are difficult to rinse if they dry on metal surface and then may cause trouble in subsequent plating operations if they are not completely removed during rinsing. Silicates should not be in cleaning solution if electrolytic bright nickel and copper plating follows, or if a subsequent hot processing is used when glassy silicate films may form on the surface.

- Carbonates

Carbonates are a cheap source of alkalinity and because they have not as strong adherence to metal surface as sodium- or potassium-hydroxide and because of their lesser corrosion behaviour, they are alternatives to alkali-hydroxides. They act as a buffer and an absorbing media for the liquid components of the cleaner. Hydroxides are another relatively inexpensive source of strong alkalinity. Borates are somewhat like silicates in that they provide some detergency, act as a buffer, and provide some metal protection, but are in general more expensive.
- Additives

Additives are either organic or inorganic complexing compounds that provide additional cleaning or surface modification. Chemical compounds such as glycols, glycol ethers, chelating agents, and polyvalent metal salts could be considered additives. The complex soluble metallions prevent deposition during electrolytic cleaning. For environmental reasons, chelating agents are replacing phosphates in some cleaning formulas. These additives can soften water and complex or tie up metal ions. Some widely used chelating agents include: sodium gluconate, sodium citrate, tetrasodium ethylenediamine tetraacetate (EDTA), trisodium nitrilotriacetate (NTA), and triethanolamine. Because EDTA and NTA cause trouble in waste water treatment too, these ingredients in metal cleaning solutions nowadays are barely used.

- Surfactants

Surfactants are very important organic compounds which provide detergency, emulsification, and wetting in an alkaline cleaner and increase stability of cleaning solution. There are four major types of surfactants:

- **Anionic:** Sodium Alkylbenzene Sulfonate
- **Cationic:** Quaternary Ammonium Chloride
- **Non-ionic:** Ethoxylated Long Chain Alcohol
- **Amphoteric:** Alkyl Substituted Imidazoline

A typical anionic surfactant is sodium dodecyl sulfonate: the anionic (active) group is \( \text{C}_{12}\text{H}_{25}\text{O}^- \) balanced by \( \text{SO}_3\text{Na}^+ \). The cationic type is represented by trimethyl dodecyl ammonium chloride in which the active cationic group is \( \text{C}_{12}\text{H}_{25}\text{N(CH}_3\text{)}_3^+ \), balanced by the simple chloride ion \( \text{Cl}^- \).

Non-ionic surfactants are of many types; a typical one is polyethylene oxide \( (\text{CH}_2-\text{CH}_2\text{O})_{10}\text{H} \).

Anionic surface-active agents (surfactants) are used in electrolytic cleaning solutions, while combinations of non-ionic (low-foaming) and anionic surfactants are added in immersion and spray cleaning solutions.
Electrolytic Cleaning

An electrolytic cleaning operation usually follows an alkaline degreasing and serves two purposes:

- Electrolytic cleaning removes residual soils that may have been left behind by a degreasing step.
- Electrolytic cleaning in the cathodic mode activates the metal surface by eliminating the passive condition.

A certain direct current (2-12 V) is applied to yield current densities ranging from 1 to 15 A/dm². In the case further electroplating is required, workpieces are after electrolytic cleaning usually pickled in mineral acids or solutions of proprietary acid salts, which neutralise any residual alkali film. This treatment also remove oxides and smuts and activate the surface for subsequent electroplating.

But it is important to know that quality and adherence of the final electroplating finishing depends on the whole pretreatment process including degreasing and alkaline electrolytic cleaning. Electrolytic cleaning is not limited on following electroplating processes, it is also used in other metal finishing processes such as phosphating, chromating and painting, with respect to a greater degree of cleanliness.

The selection of electrolytic cleaner, its use concentration, temperature, time and polarity depend on three major considerations:

- Substrate to be cleaned
- Nature of soil
- Type of final plating process

Metal substrates that are commonly electrolytic cleaned include steels, copper and its alloys, nickel and its alloys, and zinc die castings. Electrolytic cleaning can be performed in rack, barrel and continuous strip operations. It is well-known that alkaline cyanide-plating solutions like copper electrolyte are not as critical to cleaning as noncyanide electrolytes, largely because the plating solution it-
self is acting as a cleaner. For such processes cleaner selection is easier. On the other hand several plating solutions like acid chloride zinc or nickel electrolytes does not tolerate soiled workpieces or oil drag-in. For them, type of cleaner and cleaner efficiency are much more important. Especially certain compounds like silicates and gluconates used in formulating cleaning solutions causes problems if dragged into such plating solutions.

- Anodic Electrolytic Cleaning

Also referred to as reverse current cleaning, anodic electrolytic cleaning is used most widely on ferrous metals. Because the workpiece is actually the anode (positive), free electrons are discharged by the hydroxyl ions to the metal, resulting in the liberation of gaseous oxygen. The oxygen bubbles liberated at the workpiece create a scrubbing action, which actually blasts dirt particles off the workpiece. These bubbles rise to the top of the cleaner, increasing solution agitation and continually bringing fresh cleaning solution to the workpiece. The bubbles act as a buoyancy raft to suspend soil which can be skimmed off or overflowed to waste.

Anodic electrolytic cleaning is desirable in the preplate cycle because the positive charge creates an oxidising condition at the metal interface. This may remove metallic oxides and smuts, but also prevents the deposition of other positively charged metallic ions, which otherwise may result in a detrimental film on the work-piece that usually is undetectable until after electroplating. It also prevents hydrogen embrittlement during cleaning, which is important for high-strength steels.

Nonferrous metals, such as zinc die castings, copper, and brass, may be successfully cleaned anodically; however prolonged times, high temperatures and high current densities must be avoided to prevent etching, pitting and dezincification of brass.
Because these nonferrous metals may be oxidised because of oxygen liberation, specially formulated cleaning compounds containing inhibiting additives are used.

- Cathodic Electrolytic Cleaning

Direct current, or cathodic electrolytic cleaning, employs a negative charge on the part. The cleaning action obtained is somewhat better than that of anodic cleaning because hydrogen gas is evolved at the cathode (workpiece), and at a given current density, twice the volume of hydrogen is liberated at the cathode than oxygen at the anode. The added mechanical scrubbing action and solution agitation, coupled with the fact that the negatively charged workpiece repels negatively charged particles of soil, are the major advantages of cathodic cleaning. The electrons are supplied to the cathode where they combine with positive hydrogen ions to liberate hydrogen gas.

A disadvantage of cathodic electrocleaning is that the negatively charged workpiece attracts positively charged species, including metallic ions such as copper and zinc and other species such as soaps and colloids. These particles may plate out onto the workpiece, producing a loosely adherent film that can lead to subsequent electroplating problems. Problems may include blistering, poor adhesion, roughness, etc. For this reason, cathodic cleaning usually is not used as the final step in the preplate cycle. Another disadvantage of cathodic cleaning is hydrogen embrittlement. Certain steels may become embrittled due to the occlusion of gaseous hydrogen.

Alkaline electrolytic cleaners are formulated from a carefully selected combination of alkalis, wetting agents, soaps, and chelators. The presence of amounts of certain compounds must be adjusted depending on the substrate to be cleaned.
Components of Electrolytic Cleaner

- Sodium Hydroxide

Sodium hydroxide is one of the most important ingredients in alkaline electrolytic cleaners. It offers a high amount of alkalinity and is the most conductive. Among the disadvantages of sodium hydroxide are poor soil removal (especially on the non-saponifiable soils) and difficulty in rinsing. Lesser amounts of sodium hydroxide are incorporated in non-ferrous metal cleaner formulations to minimise substrate attack.

- Carbonates and Sodium Carbonate

These two substances are low-cost sources of alkalinity and offer good buffering and water softening, but their major purpose in dry mix cleaners is as a carrier for liquid surfactants, which yield a clump-free, free-flowing powder. High carbonate contents are used in non-ferrous metal cleaner formulations because they buffer well at lower pH levels.

- Silicates

Silicates are usually present in most heavy-duty alkaline electrolytic cleaners because they act as pH buffers and offer good wetting, emulsifying and deflocculating characteristics when compounded with surfactants. The most common silicate used is sodium metasilicate (Na$_2$SiO$_3$). It is used both in the anhydrous form and as pentahydrate and can be an effective anodic inhibitor for certain non-ferrous metals. Another silicate is sodium orthosilicate (Na$_4$SiO$_4$) which is widely used in cleaning solutions for steel. Silicates as compounds of metal cleaner are a somewhat controversial subject because they are difficult to rinse and can cause trouble in following plating operations. Therefore some process specifications call for non-silicated cleaners.

- Phosphates

Phosphates are good water softeners and aid in sequestering (dispersion or peptization of soils) and chelation. The most common phosphate used is sodium tripolyphosphate (Na$_5$P$_3$O$_{10}$). Disodium phosphate (Na$_2$HPO$_4$) is used for buffering in the pH range of 8 to 10. Tetrasodium pyrophosphate (Na$_4$P$_2$O$_7$) is a
good sequestrant for zinc, copper and magnesium but it is not very soluble. Phosphates also aid in buffering, add alkalinity, improve ability to rinse and control of scale. Because of their controversial influence on environment (eutrophoric behaviour) phosphates in the past they are replaced by chelators (sodium gluconate, sodium citrate, etc.) or other water softeners which convert the otherwise insoluble calcium or magnesium salts into free-rinsing precipitates. Today, many phosphate-free cleaners are available that are as effective in cleaning as their phosphated counterparts.

- Surfactants

Surfactants which are usually either non-ionic or anionic in charge, provide the required wetting and dispersing properties at the operating pH of the cleaner. Care must be taken in formulating to limit their concentration because they may become in-soluble and float to the top assume if cleaner concentration is high. Surfactants used in electrolytic cleaning are commonly of the non-ionic detergent type in conjunction with an anionic coupling agent. Surfactants decrease surface tension (improve wetting) and improve detergency. Most widely used surfactants in electrolytic cleaning solutions are sodium linear alkyl sulfonates and fatty alcohol sulphates.

- Rinsing

A good water rinse is essential for good cleaning. The water rinse may be either hot, warm, or cold, but it should be kept relatively clean. In order to ensure good rinsing, the water rinse should contain no more than a certain amount (3%) of the concentration of the cleaner solution. The cleaner conditions the soil and the water rinse removes it. However, in most cases the water rinse is used to remove the cleaner solution and perhaps a minor amount of soil. Water rinsing can usually be done by using either immersion or spray. Warm is usually the best temperature for a water rinse. Furthermore jetting, agitation etc. are effective in eliminating the last traces of low surface tension cleaner constituents, e.g. silicates.
2.6 Methods for Testing Surface Cleanliness

Various methods have been developed to measure different types and sometimes very specific contamination on metal surfaces [2, 16, 18, 63, 76, 97]. Nevertheless at present very few quantitative cleanliness measurements are available. Most of the test methods are qualitative or semiquantitative. Quantitative methods are normally very complicated and hard to adapted to production processes. However a combination of different methods is normally required in order to get a complete picture of the different types of surface contamination.[97-101]. In order to be of direct use to the production line a measurement method requires a combination of characteristics. It must be easy to use without specialist competence, not very special type of equipment, reliable enough to give reproducible results and at the same time rapid and cost effective.

2.6.1 Indirect Tests

The indirect tests methods can be devided in two principal groups of test methods. The first group describe effectivity of cleaning treatment by analysis the cleaning solution. The second group describe the cleanliness of a surface by the analytical investigation of special solutions where the workpieces are diped after the pretreatment procedure.

Extraction of the washing and analytical methods like atomic absorption spectroscopy (AAS), inductive coupled plasma spectroscopy (ICP), infrared spectroscopy (IR), ion cromatography, etc. are required to measure the amount of soil after immersion the contaminated samples in special solutions. The solution must be able to dissolve impurities. Alcohols, chlorinated hydrocarbon and other organic solvents are wellknown.

In the electronic industry sometimes the IPC acetonitrile test is used [16, 102]. It is a two-stage test which may allow certain contaminants to be detected or identified. The test consists of running a few drops of acetonitrile over an area of the circuit under test. This is collected on a clean microscope slide and allowed to evaporate. A visual examination will give an initial idea as to whether any contamination has been washed out.
2.6.2 Direct Tests (Test of Metal Surface)

Visual Judgement

☐ Wiping Methods

These test methods are very simple and for qualitative visual judgement [18,63,76,97,103,104]. Because of the nature of this type of test only coloured soil is provable and the contamination must be very heavy. Furthermore, visual inspection of a surface that is not bright and smooth is of little use. If the sample is coated with pigmented soil, cleaned and then wiped with a white linen cloth or paper, presence of soil on the cloth or paper indicates poor cleaning. Colouring the surface with nigrosine powder as an indicator makes this test method more effective [76].

In some cases a similar test method is done with a tape impression on the sample instead of the white cloth [73,103]. The adhering pigments can be count later on a white paper or by recording the change in optical transmission with a densiometer when using a transparent adhesive tape [16,103]. Evaluation can be enhanced by light microscopy. Disadvantages of all these types of test methods is the fact that only low adherent contaminations can be detected. Thin layers of oxide films, or grease, or release agents are not seen.

☐ Fluorescent Method

This test requires fluorescent mineral oils or greases and expect the sample in a dark room with a suitable UV-light source [76,97,103,104,105]. Typically, UV radiation at 365 nm wavelength is used. Greases (mainly animal and vegetable) which do not fluorescence, will reveal the presence of dyed contamination (hydrocarbon soluble indicator) or the absence of a dyed product, such as a conform coating. Fluorescent method is very slow and less sensitive than the water-break and atomizer tests.

☐ Acid Copper Test

For the acid copper test the workpieces must be made from a material electrochemical unnoble in an acid sulphuric acid solution in comparison with copper (e. g. iron) [105,106].
The sample is immersed in a copper sulphate solution of copper sulphate and of sulphuric acid. On surface areas free from impurities copper will be deposited by chemical activity. If cleaning conditions are optimised the copper deposits form a strongly adherent, semi-bright deposits free of pores. An important disadvantage with this method is that parameters other than surface contamination can affect the coating, and there is a time delay for the results with respect to production.

**Nielson Method**

This test method is a combination of water-break test and acid copper test [107,108]. Ten soiled samples were first individually checked by the water-break test and then exposed to acid copper test. An average of the times required to clean the ten panels is taken as a measure of the effectiveness of cleaning conditions.

**Particle Counting**

If the metal surface is contaminated with particles in principle these particles down to about 5 μm can be counted. They can be counted either direct on the surface of the sample or after an extraction using ultrasonic agitation. The water is filtered and the particles on the filter are sized and counted under a microscope [76,97,103]. With respect to the size of the particles several methods of optical inspection may be used, ranging from the naked eye through to sophisticated electron microscope. The same as the methods described above optical inspection with the naked eye or lower magnification (2-100x) is not very precise. Particle counting with the support of a scanning electron microscope (SEM) is lengthy and cost intensive and only small parts of the sample can be controlled.

**Wetting and Surface Tension Measurement**

A clean surface has a high surface energy and can be wet by a liquid (water) if the resultant surface has a lower total energy. The presence of soil (oils, greases, etc.) prevent formation of a thin uniform water film. The water strives to
break up into discrete droplets, thereby reducing its surface area and increasing the exposed surface area of the low surface energy substrate. Simple tests like the water-break test or the atomizer test are often used although the received results are often inaccurate. Surface tension, contact angle and wetting balance measurements are more accurate but this techniques require a specialist competence and higher costs.

**Water-break Test**

The test consists of dipping the sample into clean water to reveal a break in the water film in the soiled area. It is a very simple test widely used in industry [104,109-113] because this test is very fast (5-60 s). However, because the test depends on the thickness of the applied water film, a factor which cannot be controlled, false results can be obtained because of bridging of residues. A mild acid dip before testing for water break has been found advantageous [97].

**Atomizer Test**

To make the water break test more sensitive the atomizer test was created [100,101,114]. In the atomizer test samples are cleaned, acid dipped, sprayed with an atomizer containing a blue dye solution. Just before the droplets begin to run, the spray is stopped and the sample is placed in a horizontal position [76,97,114]. Heat is applied to stabilise the sample. The cleaning index is the percentage of the total area that appears clean. This is determined by placing a grid over the sample, estimating the cleaning for several random squares and then averaging for the reported value. The atomizer test is 10 to 30 times as sensitive as the water-break test but both test methods are sometimes problematic because adsorpt impurities (surface interactions) can adhere on the surface and pretend e. g. good wetting conditions on oil contaminated surfaces [97]. In general all these test methods are not precise or quantitative and give only an idea of the content of contaminants on metal surfaces after cleaning procedure. On the other hand these methods are relatively fast, cheap and practical under productions conditions, because there is no need of special types of equipment and trained personnel.
Surface Tension, Contact Angle and Wetting Balance

These methods are to apply a single drop of ultra pure water onto the metal surface and to examine the dihedral contact angle. This method was proposed first by Young [16] in the 19th century and the idea is that the dihedral contact angle only depend on the liquid surface tension and the solid surface tension. Recent publications [115-118] assume that the dihedral contact angle will vary considerably according to the volume of liquid in the drop. However there are many sources of error which means that each method must be evaluated for application to each specific cleaning process. Then for different forms of surface tension and wetting measurements can give an acceptable result.

Radioactivity Measurement

Radioisotope Tracer Technique

This method requires that radioactive atoms be mixed with the soil [119-124]. Samples are coated uniformly with the soil, and their radioactivity is determined. The samples are then subjected to various cleaning conditions after which their radioactivity is again determined. The cleaning ability of different cleaning conditions can be evaluated by the amount of radioactivity remaining on the sample. The radioisotope tracer technique is a very sensitive test but dealing with radioactive materials limit applications.

Weighing (Gravimetry)

Weight of Residual Contamination

This method is also an evaluation of cleanliness. The sample can either be weigh before cleaning treatment occur and re-weigh after finished or the sample is dipped and washed in a pure solvent (acetonitrile or isopropanol) after cleaning procedure. The amount of contaminants is then characterised by the weight of the evaporated washings. For specific applications this simple method can provide satisfactory results but a high content of contamination can remain undetected [76,07,103,104]. A second method is to place the workpiece in
an inert atmosphere oven and heat to around 250 °C to drive off the organic contaminates, monitoring the weight change. As with all extraction techniques this method measures only an average contamination level whereas local concentrations can not be estimated.

Electrical Methods

Electrical methods like conductivity measurement, surface insulation resistance measurement and surface resistance tests are often used within the electronic industry and some of these methods could be adapted for use in production line [16,113] also in other parts of the engineering industry at an acceptable cost. In the case of solvent extract conductivity measurement an efficient ionic solvent (pure water or a mixture of iso-propylalcohol and water) is used in attempt to remove all residual ionic contamination. Change in electrical conductivity of the solvent is measured being proportional to the concentration of dissolved ions. A big disadvantage of this kind of conductivity measurement is the fact, that only the ionic contamination washed off, not that left on the test object is determined.

Other Methods for Testing Surface Cleanliness

On steel surfaces important elements, like Ca, Cl, P and Si can be estimated by using a X-ray spectrometric method [125]. A non destructive method for surface contamination quality monitoring by optically stimulated electron emission (OSEE) technique is also reported [127]. Spectroscopic, electron- and ion-microscopic methods have, in most cases, a more than satisfactory detectability for relevant contamination contents. Unfortunately these methods also have disadvantages such as a high price, complicated handling procedures and demands for ultra high vacuum. On the other hand several methods such as Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy (XPS), laser ionisation mass analysis (LIMA) and ionic sensitive spectroscopy (ISS) are so sensitive to the surface that the sample must be sputter cleaned in a vacuum.
chamber before analysis. Therefore these methods are mainly used for research purposes and their use is strongly limited for surface analyses of oil and grease contamination. But they are very suitable for the analysis of oxides and difficult soluble salts.

Combustion methods and several types of infrared spectroscopic (IR), for example oil detectors on steel surfaces [127], and ultraviolet spectroscopic (UV) methods are applicable for the analyses of surface carbon contamination. However the problem is again the high equipment cost.
3 Experimental Techniques

3.1 Three Electrodes Measurement Methods

Since surface phenomena and many other interaction phenomena on a metal surface can be explained in terms of electrochemical reactions, it follows that electrochemical techniques can be excellent tools to study these phenomena [128-134].

A typical electrochemical equipment for such measurement methods include in principle first the sample (working electrode) and the solution which the sample is to be tested. A reference electrode (commonly either a silver/silver chloride electrode or a calomel electrode) contacts the solution via a salt bridge tube (Luggin-Haber capillary).[135] Luggin-Haber capillary minimises the iR drop caused by the electrolyte without significantly disturbing the current distribution on the sample [136,137]. Finally a counter electrode (glassy-carbon, platinum or other inert materials) is used to supply the current flowing at the working electrode during the experiments. All electrodes are connected with a potentiostat, which performs two main functions [138-141]:

- Control of the potential difference between the reference electrode (RE) and the working electrode (WE)
- Measurement of the current flow between the working electrode (WE) and the counter electrode (CE)

The potentiostat makes also the values of applied potential and current available to a computer for subsequent analysis. In addition most of the potentiostates are capable of measuring open circuit potential.

The basis of the three-electrode system is that the third electrode, the reference electrode, is first not polarised, since no current flows through it and secondly it can be placed geometrically in such a way, that the possibility of ohmic error is minimised [143,144]. Principle types of methods are the following:

- Galvanostatic (Constant Current)
- Potentiostatic (Constant Potential)
- Potentiodynamic (Current versus Potential)
- Open-Circuit (Potential versus Time)
3.1.1 Potential versus Time Measurement

The determination of an electrode potential versus exposure time relationship is one of the most fundamental measurements in electrochemistry. [145-147]. This simple measurement of the potential of an electrode at open-circuit can be useful in case chemistry of the system is not totally unknown. Otherwise variations of potential with time can be hard to explain.

Open-circuit measurements made in the absence of a current flow may be used under equilibrium conditions to describe the thermodynamics of an electrochemical system [131]. In opposite of this, current versus potential relationships may be used to describe the kinetics of an electrode process [128-134].

The potential of an electrode is always measured or stated with respect to a reference electrode (RE), the latter having a known, stable and reproducible potential. The electrode potential is measured as the potential difference between the working electrode (WE) and the reference electrode (RE). In order to obtain such measurements, the electrodes must be in ionic contact and the potentiostat must have a high impedance (typically $10^{10}$ to $10^{12}$ Ohm) so that the potential difference between the electrodes does not change during experiment. Exposure time could be one hour to several days. The resulting curve is a plot of the measured potential versus time [167].

A common application of this measurement method is related to redox-type electrodes which can either directly or indirectly, defines electrode potential in terms of the concentration of one or more species in solution [128-134]. Another experimental approach is involved in recording open-circuit potentials either immediately after cessation of current flow or immediately prior to current flow. These measurements normally in the millisecond range are a type of non-steady-state kinetic measurement, leading to data on rate constants and/or double-layer capacitance values [147].
In the field of applied electrochemistry there are two main applications of OC electrode potential measurements:

- Free potential measurement to provide information on the time-depend activity of a metal surface (corrosion)
- Transformation of the potential of various speciality electrochemical sensors into measurements of parameters such as pH, metal-ion concentration, dissolved oxygen level, fluoride or cyanide ion concentration using ion-selective electrodes.

Studies of corrosion phenomena with open-circuit potential/time measurements are applications related to the passivation process on metals where oxides are formed. For example stainless steels, nickel, titanium and several alloys, which form an oxide film in their normal state [148-150]. If such alloys will be immersed in aqueous solutions this oxide film can increase and causes therefore a greater corrosion protection.

Open-circuit potential measurement can also be useful in investigations of metallic coatings. Examinations of deposit behaviour of electroplated metals and alloys like zinc, cadmium, tin, copper and noble coatings (gold, silver and platinum) are very numerous [148-153]. The principle behind this method is that when two metals are coupled together in an electrolyte, they take up a mixed potential subject to the active area of each of the compounds.

### 3.1.2 Potentiodynamic Polarisations Measurement

Measurement of current/potential relations under carefully controlled conditions can yield information both on surface behaviour and on coating behaviour [132,133,154]. These techniques allow study of the effects on a electrode surface, like the influence of inorganic or organic films, passive and oxide layers, metal reduction, hydrogen and oxygen adsorption/desorption processes and other important reactions [155-158].

Anodic current density/potential curves are well-known and used in corrosion measurements. For this The National Association of Corrosion Engineers (NACE) and the American
Society for Testing Materials (ASTM) have accepted several electrochemical corrosion methods as routine procedures [159-161]. Cathodic techniques are often used to determine metal deposition and electrolytic characteristics of metal ions or other specimens in aqueous environments.

In principle potentiodynamic cathodic or anodic polarisation is the characterisation of a metal surface or/and the layer close to the surface (double-layer) by its current potential relationship [162,163]. The potential of the sample is scanned slowly in the positive (anodic) or negative (cathodic) going direction and therefore the sample acts either as a cathode or as an anode such that metal, hydrogen or other compounds (including organic compounds) are reduced or deposited on the surface or, during anodic treatment, dissolution or oxidation of the sample by forming an oxide coating take place [162-164].

Potentiodynamic polarisation measurements are relatively rapid measurement methods. A complete current/potential plot of a sample can be measured in a few hours, or in some cases in a few minutes. Investigations such as passivation tendencies and effects of inhibitors or oxidisers on the metal surface can be easily performed with this technique [164,165]. With this knowledge electrochemical characteristics of different substances in aqueous solutions can be compared on a rational basis [166,167].

3.1.3 Tafel-Plot Measurement

This technique is a special current/potential measurement method and mainly used to measure corrosion current, so that corrosion rate of a metal can be calculated. A Tafel Plot can yield the anodic current directly or it can yield the Tafel constants [168-170]. Tafel constants can then be used with the polarisation resistance value to calculate corrosion current [167].

Tafel slope of the straight line portion of a polarisation curve usually occurring at more than 50 mV from the open circuit potential, when presented in a semi-logarithmic plot in
terms of volts per logarithmic cycle of current density (commonly referred to as volts per decade) [166, 167].

The Tafel plot is normally generated by beginning the scan at the open-circuit potential and scanning to either -250 mV versus open-circuit potential (cathodic Tafel Plot) or +250 mV versus open-circuit potential (anodic Tafel Plot). It is also possible to obtain both Tafel Plots in a single scan. But in this case there is a possibility, that the negative portion of scan will alter the surface of the sample and thus change its characteristics during the positive portion of the scan [171]. Typically scan rate is 0.1 mV/sec. The resulting curve is a plot of the applied potential versus the logarithm of the measured current [166-167].

3.1.4 Polarisation Resistance Measurement

This technique is used to measure the polarisation resistance. Polarisation resistance (Rp) is defined as the resistance of the specimen to oxidation during the application of an external potential. The corrosion rate is directly related to the Rp and can be calculated from it. For this reason these techniques are very common in applied corrosion measurement [166-172]. Equivalent to the Tafel plot measurement potential is scanned from either -20 mV versus open circuit potential to +20 mV versus open-circuit potential during polarisation measurement. The curves plots the applied potential versus the measurement current. The scan rate is typically 0.1 mV/sec. [166, 167].

3.1.5 Potentiostatic Measurement

This technique applies a constant potential to the metal solution interface and measures its electrochemical behaviour as a function of time. The curves plots the applied potential versus the measurement current [128, 131, 132, 166].

Potentiostatic experiments can be used to determine diffusion coefficients of dissolved materials in a solution, to measure passivation or repassivation potentials rates and to evaluate anodic or cathodic protection techniques. A potentiostatic scan begins at a programmed initial potential and steps to a programmed final potential. The final applied potential is
maintained for a specified period of time. The current flowing as a result of the applied potential is plotted as a function of time [166,167].

3.1.6 Galvanostatic Measurement

This technique impresses a constant current upon the metal/solution interface and measures its electrochemical behaviour as a function of time. Galvanostatic measurement are used to measure passivation rates, evaluate cathodic or anodic protection techniques, or estimate the thickness of passive films or electroplated layers [128,133,134]. In the galvanostatic technique, the impressed current or current density is typically stepped from an initial value to a final value after a specified initial delay. The final current is then maintained for a specified period of time. The sample potential is continuously monitored during the process.

3.2 Electrochemical Impedance Measurement Method

Impedance measurement methods offer a convenient way of evaluating the performance of organic coating/metal systems. They provide both quantitative kinetic and mechanistic information which make them useful tools for description of electrochemical systems [146,173-175].

The simplest type of electrochemical processes is the uniform dissolution (corrosion) of a metal specimen consisting of two simple electrochemical reactions on a double layer [146]. For example the corrosion of a metal in an acid solution (i.e. zinc in HCl) can be represented by a simple resistor. The double layer is created by the voltage changes across the interface. On the metal side of the interface, there may be an excess (or deficiency) of electrons. This excess (or deficiency) is normally balanced on the solution side by opposite charged ions. Some of the ions are specifically adsorbed at the surface (inner layer) others are non-specifically adsorbed and are hydrated. They extend out into the solution in the diffuse layer. The response of this interfacial structure to varying voltage can be modelled by the double layer capacitance [175,176].
For this simple electrochemical process the model circuit is known [178,179]. The circuit is a resistor in parallel with a capacitor and the entire parallel circuit is in series with another resistor. The utility of this model for the frequency response lies in the fact that this resistor equals the solution resistance not compensated by a potentiostat and the resistor parallel with the capacitor equals the polarisation resistance as long as the measurement is made at the open-circuit potential (corrosion potential). By combining this resistor with the Tafel slopes for the half-cell reactions by an equation such as the Stern-Geary equation [170] corrosion rate can be calculated [168]. Thus analysis of the electrochemical impedance enables the corrosion rate to be estimated rapidly in the absence of uncompensated solution resistance [180-184].

Unfortunately most of the electrochemical processes are not as simple as the example just discussed [185]. Chemical reactions can be influenced by diffusion of one or more reactants or products to or from the surface. This situation can arise when diffusion through the surface film or hydrodynamic boundary layer becomes the dominating process. A surface could be covered with reaction products of limited solubility, oxides could be created, or adsorption of organic compound take place. In most of the cases the resulting film is inhomogenous and porous. When a metal is coated with a porous non-conducting film, the equivalent circuit must simultaneously account for the resistance of the system, caused by the process on the coating layer and additional the pore resistance. Two or more time constants can arise for this process, such as multi-step reactions, in which both steps have comparable rates, or an adsorbed intermediate, among other. These phenomena require more complex equivalent circuits. Nevertheless under certain circumstances description of the electrochemical mechanism might be possible by comparison with appropriate models or in the case when impedance response is characteristic for known phenomena like, Warburg impedance. New and versatile software make it easier to detect.
3.3 Two Electrodes Measurement Methods

3.3.1 Principle and Difference to Three Electrodes Measurement Method

Additional to three-electrode techniques electrochemical measurements can also be made with two electrodes. Working electrode (sample) is together with a second electrode immersed in a solution and its potential could be measured without any passage of current from an external circuit \([132,134]\). This simple recording of the rest potential may suggest what kind of processes on the surface do or do not occur.

If current is passed through a electrochemical cell (two electrode cell) the cell voltage is given by:

\[
E_{\text{cell}} = E_{\text{rev}} + \eta (\text{anode}) + \eta' (\text{cathode}) + iR
\]

Cell voltage \(E_{\text{cell}}\) is the sum of the cell reversible potential \(E_{\text{rev}}\) and \(\eta\) and \(\eta'\) are the anode and cathode overvoltages. The ohmic drop \(iR\) is given by the electrolyte. \(E_{\text{rev}}\) can be measured and/or calculated, and then subtracted out from the right-hand side of the equation. If one of the electrodes is much larger than the other (\(x\) 10 preferably \(x\) 100 in terms of true surface area) overvoltage of one electrode can usually be neglected in relation to the overvoltage at the smaller one, because current density at the surface is much higher. The resistance of the electrolyte is also neglected if an electrolyte of good conductivity is used. Under such certain circumstances two-electrode measurement can be an useful tool for electrochemical techniques \([146,166,167]\).

For example this measurement method is in principle the basis of the well-known and often used polarographic techniques, where a small dropping mercury electrode is used in conjunction with a much larger mercury pool \([129,133,134,146,155]\). On the other hand cell voltages \(E_{\text{rev}}\) can be reduced to an expression where the only unknown term is the sum of the two overvoltages.
3.3.2 Galvanostatic Measurement

Similar to galvanostatic measurement with the support of a potentiostat (3.1.6) this technique impresses a constant current upon the metal/solution interface and measures its electrochemical behaviour as a function of time. Because of the absence of the third electrode this technique is based on two circuits that are wholly independent of one another [134]. The first is the current circuit, which connects working electrode and counter electrode to a constant current source. The second circuit, measurement circuit, connects working and reference electrodes to a potential/measurement device (voltmeter). From these, a current/voltage plot via a xy-plotter or a computer is possible.

This measurement method is a very simple and robust one and can record many surface phenomena if care is taken on some typical characteristics.

Using very low currents, (less than 10 μA) a potential measurement device with low impedance (1 Mohm or less) would introduce errors, as the current in the measurement circuit forms a significant part of the total current. Therefore multimeter with impedance of 10 MOhms or more are necessary [166,167].

When the shape of the current/voltage plot exhibits a maximum and minimum (passivation or inhibitor phenomena), one particular value of current can be observed at three different potentials and this type of galvanostatic method will fail to resolve this.

3.3.3 Contact Current (Contact Corrosion) Measurement

The differences in electrochemical potential between two metals in electrical contact (galvanically coupled together) in an electrolyte cause electron flow between them; commonly called a corrosion current [116,117]. In principle this current can be measured with the two-electrode measurement technique, but response either from the anodic or the cathodic electrode during exposure can change the measurement conditions and causes current errors.
4. Experimental Results

4.1 Introduction

Electrochemical techniques theoretically should provide some of the more sensitive methods for measuring the activity of metal surfaces. Usually they are used under accurate and carefully prepared experiments under laboratory conditions. But in order to develop a quality control technique for monitoring process cleaning under production conditions measurement techniques must be simple and robust. Therefore, the main object of the following examination was to show the principle possibility of a simple, effective and robust two-electrode measurement cell to estimate cleanliness of metals. To examine the level of accuracy and detectability of this kind of measurement several electrochemical and other than electrochemical methods were combined.

4.2 Experimental Apparatus and Techniques

Measurements with the three-electrode techniques were made with a potentiostat (273A, EG&G, Princeton/NJ, USA) connected with a lock-in-amplifier (521, EG&G, Princeton/NJ, USA) for impedance measurements. Evaluation of the resulting curves was done with the support of commercial software (PAR M352 Rev.2.01 and PAR M398 Rev.1.01, EG&G, Princeton/NJ, USA).

To isolate the reference electrode from the sample solution a salt bridge (Luggin-Haber capillary) containing noninterfering ions (saturated KCl gelled with agar) was used. Reference electrode was a calomel-electrode (SCE, $E_{pot} = 241.5$ mV). Counter-electrode was a glassy carbon electrode. Earlier investigations have shown that this type of electrode does not influence the measurement conditions.

During two-electrode measurements a cell of size equal to coulometric measurement cell was used. The two electrodes were connected via a multimeter with a high impedance (197A, KEITHLEY, Cleveland/Ohio, USA) to a xy-plotter (KIPP & ZONEN, Delft, Netherlands). The Counter-electrode was a stainless steel tube which allows to put reference electrode inside for further three-electrode measurements. Basic circuit diagram
of the measurement cell and a schematic voltage versus time graph are shown in figure 1.

![Figure 1: Typical Potential / Time Curves at Constant Current]

Basic Circuit Diagramm

Figure 1
Two Electrode Measurement Method to Estimate the Degree of Coverage and typical Voltage/Time Curves
The solution containing 10 g/L KOH was prepared from reagent grade potassium hydrogen (MERCK, Hohenbrunn, Germany). NaCl solution (MERCK, Hohenbrunn, Germany) and Na₂SO₄ solution (FLUKA, Buchs, Switzerland, Germany) were prepared by adding buffers. Buffer pH = 7 was a mixture from KH₂PO₄/Na₂HPO₄ (RIEDEL-DE HAEN, Seelze, Germany) and buffer pH = 4 was made by adding potassium hydrogen phthalate (C₈H₅KO₄, MERCK, Hohenbrunn, Germany). Sodium persulfate (Na₂O₈S₂, FLUKA, Buchs, Switzerland) was used to activate copper surfaces and potassium cyanide (KCN, MERCK, Hohenbrunn, Germany) for silver activation. Degree of purity of all chemicals was "pro analyse" including different alkylthiols (MERCK, Hohenbrunn, Germany). Soil and other organic compounds were used in their typical form normally found in plating shops.

For potential versus time measurements, potentiodynamic polarisation measurements and electrochemical impedance measurements the solution was purged with oxygen-free nitrogen gas (99.99) at a flow rate of about 100 to 150 cm³/min for one hour before sample immersion. Purging was continued throughout the experiment.

After transferring the sample into the test cell the Luggin-Haber capillary was adjusted in this way so that it was less than 1-2 mm from the sample. Close placement is important since this distance will affect the uncompensated solution resistance; on the other hand, it must not act as an electrode shield.

In the case of the cell for galvanostatic measurements, the capillary is fixed adjacent to the counter-electrode (CE). Current/density potential tests (scan rate 1 mV/sec) and impedance measurements were recorded for 30 to 60 minutes, while open circuit potential measurements were recorded for 1 to 24 hours.

For impedance measurements frequency response between 10 000 Hz (KHz) and 0.1 Hz (100 mHz) at the open circuit potential was recorded after 1 hour of exposure using 8 to 10 steps per frequency decade. The amplitude was normally 10 mV.

Galvanostatic studies with two-electrode measurement cell were recorded during exposition time from 30 to 60 seconds.
For investigations on the possibility for assessing cleaning conditions for metal surfaces using electrochemical methods some typical kind of soils and materials were examined. Samples consisted of the following materials:

- **Silver**
  Bright silver coatings 2-5 μm
  on brass (Ms 67) substrate,
  from different cyanide electrolytes plated under production conditions

- **Silver (99,99)**
  as a bulk material

- **Gold**
  Hard-gold coatings 0,1-2 μm
  on silver (ECD) intermediate layer on brass (Ms67) substrate from different cyanide electrolytes plated under production conditions

- **Gold (99,999)**
  as a bulk material

- **Copper (oxygen free)**
  as a bulk material,
  for electronic industry

- **Brass (Ms67 and Ms60)**
  as a bulk material,
  for decorative use

- **Bronze (Cu-Sn)**
  as a bulk material,
  for decorative use

- **Bronze (CuSn6)**
  as a bulk material,
  for electronic industry

- **Steel**
  (SANDVIK 29 AP;
  1 %C, 15 % Si, 0.4 %Mn, 0.02 % P, 0.05 % S, 0.2 % Pb),
  for computer manufacturing

- **Stainless Steel (CrNi18/8)**
  for functional use
These materials allow to be shown the principles of change in electrochemical behaviour caused by the influence of organic compounds, oxide and passive layers, pigmented drawing oils, etc. on noble, un-noble and passive metal surfaces. Samples were examined at different state of pretreatment processes:

- **Pure State - without any Pretreatment**
  (oxides, inorganic and organic compounds on the surface)

- **Immediately after Solvent Cleaning**
  (organic compounds on silver and gold surfaces)

- **Immediately after Etching**
  (copper and copper alloys after etching in potassium sulphate solution)

- **Immediately after Alkaline Cleaning**
  (alkaline immersion cleaning with and without support of ultrasonic and electrolytic cleaning; copper, copper alloys and steel)

- **Continuous during Immersion in Alkaline Cleaners**
  (copper, copper alloys and steel)

On copper-zinc (brass) and copper-tin (CuSn6) bulk materials the removal of typical lubricants (used in factories producing contact-material for the electronic industry) with different degreasing procedures like alkaline cleaning with ultrasonic support and electrolytic immersion cleaning was examined. Different types of lubricants are summarised beyond:

- **TOWER E 103** (TOWER OIL & TECHNOLOGY Co, Chicago, USA)
  An oiliness additive extremely fluid and emulsified with all petroleum and fatty oils. Provides polar lubricating and is compounding with several rolling and cutting oils

- **RAZIOL-FS 1 S** (ZIBULL & SOHN GmbH, Iserlohn, Germany)
  A mineral oil with polar additives like sulfonate and chlorides (6.2% Cl)

- **RAZIOL-CLF 25 E** (ZIBULL & SOHN GmbH, Iserlohn, Germany)
  A mineral oil soluble in halogenated solvents plus synthetic ester-oils and stabilisators, free of aromatic substances and chloride additives

- **WYNNS DP 4053** (WYNNS FRANCE, Courbevoie, France)
  A fatty oil with chloride additives but free of halogenides
Furthermore these lubricants may also contain chloro-paraffine, sulphur, calcium, magnesium, silicates and boric acid. The results of electrochemical measurements were compared with other tests like the copper test on iron [107,108].

Additionally the state of cleanliness was estimated by other non-electrochemical measurement methods. Quality compositional analyses of substances absorbed on the metal surface were determined by Scanning Electron Microscope SEM (DSM940, ZEISS Oberkochen, Germany) fitted with an Energy Dispersive X-ray Microanalyser EDX (HNU, EG&G, Princeton/NJ, USA).

For detecting n-alkylthiols as sulphur on gold surfaces a Auger Electron Spectroscopy AES (PHI 600 PERKIN ELMER, Überlingen, Germany) was used.

Investigations on the bonding mechanism of higher mercaptans on noble metals were estimated by SIMS and Electron Spectroscopy for Chemical Analysis ESCA (PHI 530 PERKIN ELMER, Überlingen, Germany).

4.3 Potentiodynamic and Galvanostatic Studies of Organic Compounds on Silver and Gold Substrates

4.3.1 Silver Substrates

Silver as a bulk material and electroplated silver coatings (ECD) on brass were selected because these types of material have a high selectivity towards sulphur. Equal to bare gold and ECD-gold coatings they allow oriented organic monolayer films to be prepared on their surface [188-190]. They yield to study of structure and boundary phenomena and within the physical-organic chemistry of interfaces.

In a first step the aim has been to characterise the typical electrochemical behaviour of the silver surface depending to the kind of test solution. Therefore, silver as a bulk material was immersed in different solutions with different kinds of anions (OH⁻, CN⁻, SO₄²⁻, Cl⁻) and pH (4, 7, 12). To keep pH constant buffers were added to the solutions with pH = 4 and pH = 7. The typical current density/potential curves of the silver samples are shown in figure 2.
Figure 2
Anodic Current Density/Potential Curves on Silver Surface immersed in Acid, Neutral and Alkaline Solutions

Curve 1: in 1.8 M KCN (pH = 14)
Curve 2: in 0.5 M NaCl + KH₂PO₄ / Na₂HPO₄ (pH = 7)
Curve 3: in 0.5 M Na₂SO₄ + 0.05 M C₈H₅KO₄ (pH = 4)
Curve 4: in 0.2 M KOH (pH = 14)

RE: Calomel (SCE) 241.5 mV/NHE; CE: Glassy Carbon; scan rate: 1 mV/s
T: 30 °C; N₂ purging, without agitation

Open circuit potential of silver in KCN solutions is very un-noble ($E_{pot} = -920$ mV/SCE) and during anodic polarisation afterwards silver is dissolved (curve 1). Immersion in KOH, Na₂SO₄ and NaCl solutions cause an open circuit potential for silver of about -10 to -80 mV/SCE. If the samples are anodically polarised afterwards, they show different polarisation curves depending on the kind of solution.

In NaCl solution (curve 2) the anodic current density reaches a limited range caused by the formation of AgCl₂. In Na₂SO₄ solution dissolution of silver increases versus increasing anodic polarisation until a potential of about 500-600 mV far from open circuit potential is reached (curve 3).
Then interactions with $\text{SO}_4^{2-}$ compounds and the silver surface occur. Only when the silver samples are immersed in KOH solution, typical formation of silver(I)oxide and silver(II)oxide is observed (curve 4). Therefore, further investigations with silver samples were carried out in potassium hydroxide solutions (10 g/L KOH).

![Figure 3](image)

**Figure 3**

Anodic Current Density/Potential Curves on Silver Coatings (ECD) on Brass Substrate immersed in 1% KOH

Curve 1: Bare Silver Surface

Curve 2: Silver Surface covered with $n$-alkylthiol

$\text{CH}_3-(\text{CH}_2)_{15}-\text{SH}$

RE: Calomel (SCE) 241.5 mV/NHE; CE: Glassy Carbon; scan rate: 1 mV/s

T: 30 °C; $\text{N}_2$ purging, without agitation

In figure 3 typical anodic parts of current density/potential curves of bare silver surfaces cleaned in KCN-solution and silver surface covered with $n$-alkylthiol $\text{CH}_3-(\text{CH}_2)_{15}-\text{SH}$ immersed in alkaline solution (1 % KOH) are shown.
Pure silver coatings show two current density peaks at +300mV versus SCE and +600 mV versus SCE. The two peaks could be described as representing the following reactions:

\[
\begin{align*}
Ag & \rightarrow Ag_2O \\
Ag_2O & \rightarrow Ag_2O_2 (AgO)
\end{align*}
\]

This means silver is oxidised during anodic polarisation in two typical steps. In contrast to this phenomenon, on silver layers covered with an organic compound such reaction is not observed.

The typical current density/potential curves (with typical two peaks) depend on state of oxide formation on the silver surface but typical potential values, where silver(I) oxide and silver(II) oxide are measured are not influenced or even removed (Fig. 4). The current response is regardless of whether surface is covered with oxides (curve 1) or in a bare state after immersion in KCN-solution (curve 2).

Figure 4

Anodic Current Density/Potential Curves on Silver Coatings (ECD) on Brass Substrate immersed in 1% KOH

Curve 1: Silver Surface (Silver Oxide) after exposure in laboratory atmosphere for 7 days
Curve 2: Silver Surface direct after Deposition and Immersion in KCN Solution (115 g/L KCN)
Curve 3: Silver Surface covered with n-alkylthiol \( CH_3-(CH_2)_{15}-SH \)

RE: Calomel (SCE) 241,5 mV/NHE; CE: Glassy Carbon; scan rate: 1 mV/s
T: 30 °C; N₂ purging, without agitation
Under galvanostatic conditions (two-electrode measurement) similar behaviour is found (Fig. 5). While pure silver coatings show a potential about 0.5 V against a stainless steel electrode, potential of a covered (with thiol:CH$_3$-(CH$_2$)$_{15}$-SH) silver electrode increases up to 1.2 - 1.5 V (anodic current: 3 $\mu$A (17 $\mu$A/dm$^2$)). Other $n$-alkylthiols with different carbon chain-length show the same increase in potential (Table 3).

Thiols of different chain-length are important in the automobile and electronic industry because they inhibit the silver layer against corrosion attack by atmospheres containing sulphur and reduce insertion force in contrast to other treatment like chromate treatment or corrosion protection by a final treatment with thin films of a metal with higher resistance against corrosion (i.e. 0.1-0.5 $\mu$m rhodium plating).
Table 3  Open Circuit Potentials of Different Kind of Thiols

<table>
<thead>
<tr>
<th>Substrate/Layer</th>
<th>Organic Coverage</th>
<th>Potential mV/CrNi18/8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brass/ECD-Silver 5 μm</td>
<td>CH₃-(CH₂)₁₅-SH</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>Brass/ECD-Silver 2 μm</td>
<td>CH₃-(CH₂)₁₉-SH</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>Brass/ECD-Silver 2 μm</td>
<td>CH₃-(CH₂)₁₇-SH</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>Brass/ECD-Silver 2 μm</td>
<td>CH₃-(CH₂)₁₅-SH</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>Brass/ECD-Silver 2 μm</td>
<td>CH₃-(CH₂)₁₁-SH</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>Brass/ECD-Silver 0.1 μm</td>
<td>CH₃-(CH₂)₁₅-SH</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>Silver</td>
<td>CH₃-(CH₂)₁₅-SH</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>Silver</td>
<td>CH₃-(CH₂)₁₇-SH</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>Brass/ECD-Silver* 1.0 μm/</td>
<td>CH₃-(CH₂)₁₅-SH</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>ECD-Gold 0.2 μm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Solution: 1 % KOH; RE: Stainless Steel (CrNi 18/8) T: 25 °C; Surface Ratio WE:RE = 1:100; Without agitation and purging with N₂

* Argostar 500, BLASBERG, Solingen, Germany

Table 3 shows that different kinds of thiol (C₁₂ to C₂₀) do not cause any change in open-circuit potential after an exposure time of 30 to 60 seconds. Alkylthiols create films with high impedance both on electroplated silver coatings and on silver bulk materials.

Alkylthiols are so selective on silver that a similar behaviour is found on silver surfaces covered with thin ECD-gold layers (0.2 μm). Because of the porosity of thin gold coatings thiols can be adsorbed throughout.

Alkylthiols are organic compounds and therefore only recovered from metal surfaces by immersion in solvent solutions or by heat treatment. Table 4 summarises the influence of different cleaning solutions and varied immersion times of contaminated silver surfaces on their open-circuit potential.
<table>
<thead>
<tr>
<th>Organic Compound</th>
<th>Cleaning Solution</th>
<th>Immersion Time (min)</th>
<th>Potential *) mV/CrNi18/8</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solvent Cleaning at 25 °C (RT)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$-(CH$<em>2$)$</em>{17}$-SH</td>
<td>C$_2$HCl$_3$</td>
<td>1</td>
<td>1.2 - 1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td>CH$_3$-(CH$<em>2$)$</em>{15}$-SH</td>
<td>C$_2$HCl$_3$</td>
<td>5</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td></td>
<td>C$_2$HCl$_3$</td>
<td>10</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td>CH$_3$-(CH$<em>2$)$</em>{15}$-SH</td>
<td>C$_2$Cl$_4$</td>
<td>5</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td></td>
<td>C$_2$Cl$_4$</td>
<td>10</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_3$Cl$_3$</td>
<td>10</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td></td>
<td>CH$_2$Cl$_2$</td>
<td>10</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td>CH$_3$-(CH$<em>2$)$</em>{15}$-SH</td>
<td>Pentane</td>
<td>10</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td></td>
<td>Dodecane</td>
<td>10</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td></td>
<td>Isooctane</td>
<td>10</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td>CH$_3$-(CH$<em>2$)$</em>{15}$-SH</td>
<td>Methanol</td>
<td>10</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td></td>
<td>Butanol</td>
<td>10</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td></td>
<td>Isopropanol</td>
<td>10</td>
<td>0.8 - 0.7</td>
</tr>
<tr>
<td><strong>Vapour Degreasing at Boiling Point of Solvent (60-90 °C)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$-(CH$<em>2$)$</em>{17}$-SH</td>
<td>C$_2$HCl$_3$</td>
<td>1</td>
<td>0.8 - 0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>0.7 - 0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>0.6 - 0.6</td>
</tr>
<tr>
<td>CH$_3$-(CH$<em>2$)$</em>{15}$-SH</td>
<td>C$_2$HCl$_3$</td>
<td>5</td>
<td>0.7 - 0.6</td>
</tr>
<tr>
<td></td>
<td>C$_2$HCl$_3$</td>
<td>10</td>
<td>0.6 - 0.6</td>
</tr>
<tr>
<td>CH$_3$-(CH$<em>2$)$</em>{15}$-SH</td>
<td>C$_2$Cl$_4$</td>
<td>10</td>
<td>0.7 - 0.6</td>
</tr>
<tr>
<td></td>
<td>C$_2$Cl$_4$</td>
<td>10</td>
<td>0.6 - 0.6</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_3$Cl$_3$</td>
<td>10</td>
<td>0.6 - 0.6</td>
</tr>
<tr>
<td></td>
<td>CH$_2$Cl$_2$</td>
<td>10</td>
<td>0.7 - 0.6</td>
</tr>
<tr>
<td>ECD-Silver from cyanide plating solution</td>
<td>(ARGOSTAR 500, BLASBERG, Solingen; Germany)</td>
<td></td>
<td>0.3 - 0.5</td>
</tr>
<tr>
<td>Silver bulk material</td>
<td></td>
<td></td>
<td>0.3 - 0.5</td>
</tr>
</tbody>
</table>

*) Measured against Stainless Steel (CrNi 18/8) in 1 % KOH at 25 °C; Surface Ratio WE:RE = 1:100
The examples given in Table 4 show that recovery of thiol from a silver surface is hardly possible with solvent cleaners because of their strong adhesion to the surface. After immersion in cold solvent cleaners or vapour degreasing there is always a residue of organic compound on the silver layer as examined by scanning electron microscope (Fig. 6) and x-ray analysis (Fig. 7).

**Figure 6**

Adsorbed Hexadecanethiol $\text{CH}_3-(\text{CH}_2)_{15}-\text{SH}$ on ECD-Silver Layers (2 $\mu$m on Brass Substrate) determined by Scanning Electron Microscope (SIMS)
Silver covered with Hexadecanethiol \( \text{CH}_3-(\text{CH}_2)_{15}-\text{SH} \)

After Immersion in Trichlorethane \( \text{C}_2\text{H}_3\text{Cl}_3 \)
10 Minutes at RT

Figure 7
Adsorbed Hexadecanethiol \( \text{CH}_3-(\text{CH}_2)_{15}-\text{SH} \) on ECD-Silver Layers (2 \( \mu \)m on Brass) determined by Scanning Electron Microscope (SEM) and an Energy Dispersive X-ray Microanalyser (EDX); Detected as Sulphur Resonance
Investigations on the bonding mechanism of hexadecanethiol on silver using Secondary Ion Mass Spectroscopy (SIMS) and Electron Spectroscopy for Chemical Analysis (ESCA) revealed fragments of the organic compound (Ag-S-CH$_2$ and Ag-O-C) which means that adhesion is mainly a chemi-adsorption reaction (Fig 6). Otherwise hexadecanethiol would not have to break down. Thickness of the organic layer is probably about 1 to 5 monolayers. This would explain the difficulties in removing thiols from silver layers in contrast to gold layers where adsorption of thiols is described as a kind of physical-adsorption [190].

![Diagram of secondary ions and interface bonding mechanism](image)

Figure 8
Secondary Ions and Interface Bonding Mechanism between Hexadecanethiol and Electroplated Silver Layers by SIMS and ESCA Analysis
After vacuum treatment ($5 \times 10^{-6}$ bar) for 7 days at room temperature ($25 \, ^\circ \text{C}$) a silver layer immersed for 1 minute in a solution containing alkylthiol ($C_{16}$) shows a free potential of about 0.7 to 0.8 mV (Fig 9); 200 - 300 mV higher than a pure silver surface. Analyses made by ESCA and SIMS detected nearly the same amount of hexadecanethiol on the sample surface as measured without any vacuum treatment.

If the samples are exposed to a vacuum at temperatures of about 120 °C for 7 days the hexadecanethiol is removed completely and the silver layer exhibits a free potential of about 0.5 mV/stainless steel (Fig. 9).

![Figure 9](image)

Figure 9

Potential versus Time Measurement of Silver Surface (ECD-Ag/Brass) covered with Hexadecanethiol $\text{CH}_3-(\text{CH}_2)_{15}-\text{SH}$ before and after Heat Treatment

RE: Stainless Steel (CrNi18/8); Electrolyte: 1% KOH; T: 25 °C; without agitation and purging with $\text{N}_2$

These investigations support the proposition that electrochemical measurements in a simple format can be very sensitive methods for the detection of organic layers on metal surfaces. To examine the generality of the behaviour observed, many more substances on silver layers were examined using the two-electrode technique (galvanostatic measurement) as described in Table 5.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Covering Soil</th>
<th>Potential mV/CrNi18/8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>India Rubber containing Silicone dissolved in C₂Cl₄</td>
<td>1.5 - 1.7</td>
</tr>
<tr>
<td>Silver</td>
<td>Solution with Drilling Compounds</td>
<td>1.0 - 1.2</td>
</tr>
<tr>
<td>Silver</td>
<td>Human sweat &quot;Finger-Prints&quot;</td>
<td>0.6 - 0.7</td>
</tr>
<tr>
<td>Silver</td>
<td>Commercial Cleaning Solution POLYBOY (WMF, Germany)</td>
<td>0.5 - 0.6</td>
</tr>
<tr>
<td>Silver</td>
<td>Commercial Cleaning Solution for Electronic Contacts CONTACT-SPRAY (DODUCO, Germany)</td>
<td>0.5 - 0.6</td>
</tr>
<tr>
<td>Silver</td>
<td>Lubricant used in Fabrication Electronic Contacts and PC's (RAZIOL, Germany)</td>
<td>1.3 - 1.5</td>
</tr>
<tr>
<td>Silver</td>
<td>Fatty Grease &quot;Make-up&quot; creme NIVEA (NIVEA, Germany)</td>
<td>1.2 - 1.5</td>
</tr>
<tr>
<td>Silver</td>
<td>Motor-Oil for Filter-Pumps TRAFO-ÖL (EHEIM, Germany)</td>
<td>1.5 - 1.7</td>
</tr>
<tr>
<td>Silver</td>
<td>Silver Plating Solution containing KCN; ARGOSTAR 500 (BLASBERG, Germany)</td>
<td>0.5 - 0.5</td>
</tr>
<tr>
<td>Silver</td>
<td>Chromate Layer for Tarnish Protection ARGUNAT 201 (DEMETRON, Germany)</td>
<td>0.8 - 0.9</td>
</tr>
<tr>
<td>Silver</td>
<td>AgS after Immersion in Thiocyanate Solution</td>
<td>1.2 - 1.5</td>
</tr>
<tr>
<td>Silver</td>
<td>Immediately after Electroplating Bright Silver Bath with Additives ARGOSTAR 500 (BLASBERG, Germany)</td>
<td>0.5 - 0.5</td>
</tr>
<tr>
<td>Silver</td>
<td>Immediately after Electroplating Silver Bath without any Additives Silver Electrolyte from Literature</td>
<td>0.5 - 0.5</td>
</tr>
</tbody>
</table>

Test solution containing 1% KOH; Reference Electrode: Stainless Steel (CrNi 18/8); Temperature: 25 °C; without agitation; without purging N₂; Surface Ratio WE:RE = 1:100
4.3.2 Gold Substrates

Gold layers produced by electrodeposition or as bulk material show analogous behaviour during anodic polarisation as when they were covered with an organic film like long-chain thiol, except that typical maxima in current density responses are not observed because of the different electrochemical reaction in the case of gold (Fig. 10).

![Figure 10](image_url)

**Figure 10**

Anodic Current Density/Potential Curves on Gold Coatings (ECD) on Brass Substrate immersed in 1% KOH

Curve 1: Bare Gold Surface  
Curve 2: Gold Surface covered with $n$-alkylthiol  
$\text{CH}_3-(\text{CH}_2)_{15}-\text{SH}$

RE: Calomel (SCE) 241.5 mV/NHE; CE: Glassy Carbon; scan rate: 1 mV/s;  
T: 30 °C; N₂ purging, without agitation

There is a dramatic difference between the $i$-$E$ response for a $\text{CH}_3-(\text{CH}_2)_{15}-\text{SH}$ coating on gold and a bare gold surface. Results are in good correspondence with data Porter et al [190] reported in 1987. They studied $n$-alkylthiols of different chain-lengths ($n = 1 - 21$) adsorbed on gold from dilute solutions.
Using various types of measurement methods, such as optical ellipsometry, infrared spectroscopy and electrochemistry, they discovered that these thiol monolayers are excellent to use as a model system for fundamental studies of heterogeneous charge-transfer, ion transport and double-layer phenomena. But as a quick and economical method to describe the effectiveness of a cleaning process these measurement methods as used by Porter et al [190] are not very practicable.

Figure 10 shows the potential response of uncovered and covered gold surfaces during constant anodic current (galvanostatic) in alkaline solution upon the metal specimen. As expected the gold surface produces similar potential-drifts as silver surfaces.

![Figure 10](image)

**Gold covered with Hexadecanethiol (CH₃-(CH₂)₁₅-SH)**

**Bare Gold**

**Figure 11**

Potential versus Time Measurement on Pure Gold Surface (ECD-Au/Stainless Steel and on Gold surface (ECD-Au/Stainless Steel covered with an Organic Compound like Hexadecanethiol; Iₐnodic = 10 μA/dm²)

RE: Stainless Steel (CrNi18/8); Electrolyte: 1 % KOH; T: 25 °C; without agitation and purging with N₂
Potential-current response is nearly the same as that found for silver layers. In this case only a shift of the open circuit potential was found because of the different electrochemical behaviour of these two metals gold and silver. Pure gold shows a free potential of about 0.5 - 0.7 V/stainless steel; if the gold surface is covered with thiols the potential increases up to 1.7 V/stainless steel.

Additional investigations with Auger electron spectroscopy (AES) estimate a characteristic sulphur peak if gold surface is covered with alkylthiols (CH$_3$-(CH$_2$)$_{11}$-SH, CH$_3$-(CH$_2$)$_{15}$-SH, CH$_3$-(CH$_2$)$_{17}$-SH and CH$_3$-(CH$_2$)$_{19}$-SH). A typical AES profile of sulphur as a marker for n-alkylthiols created on a electroplated gold layer covered with a monolayer of hexadecanethiol CH$_3$-(CH$_2$)$_{15}$-SH is shown in figure 12.

![AES Profile](image)

Figure 12

Typical AES Profile of Sulphur as a Marker for a Monolayer of Hexadecanethiol CH$_3$-(CH$_2$)$_{15}$-SH on Gold Surface
In contrast to the behaviour on silver surfaces the adhesion of \(n\)-alkylthiol (with chain-length \(n=12\) to \(20\)) on gold layers is not as strong. After heat treatment at \(100\degree C\) for 3 to 4 hours \(n\)-alkylthiols are totally recovered. Open-circuit potential is about 500 to 700 mV/stainless steel in 1 \% KOH equal to a bare gold surface (Fig. 13).

The time of heat treatment until the gold surface is free from thiols decontaminations depends upon the chemical behaviour of these substances. A lower melting point means lower temperatures or shorter exposure times to recover \(n\)-alkylthiols (i.e. \(\text{CH}_3-(\text{CH}_2)_{15}-\text{SH}\)) from metal surfaces. Such stability of thiols on gold surface increases with an increase of chain-length of the substances (i.e. \(\text{CH}_3-(\text{CH}_2)_{19}-\text{SH}\)).

![Graph](image_url)

**Figure 13**

Potential versus Time Measurement on Gold Surfaces (ECD-Au/Stainless Steel)

Gold covered with Hexadecanethiol

After Heat Treatment, \(100\degree C, 4\) hours

\(I_{\text{anodic}} = 10\ \mu\text{A/dm}^2\)

RE: Stainless Steel (CrNi18/8); Electrolyte: 1 \% KOH; T: 25 \degree C; without agitation and purging with \(N_2\).
4.4 Potentiodynamic and Galvanostatic Studies of Oxide Layers on Copper Substrates

4.4.1 Potentiodynamic Measurement

In atmospheres containing any oxygen, oxidation of copper will occur as will sulphation if sulphur gases are present. For example, during storage or different pretreatment processes oxides on the copper surface (CuO and CuO$_2$) will be formed. These copper(I)oxides and copper(II)oxides are often of large size, coloured, hard to remove and therefore unpleasant in further treatment. Because of this, cleaning of copper surfaces means not only the removal of grease and oil but also means the chemical removal of copper oxides.

To improve the possibility of the electrochemical measurements, in the context of formation of oxides on metal surfaces, was therefore another aim of the investigations.

![Anodic Current Density/Potential curves on Copper Surface after Heat Treatment in Atmospheres containing Oxygen](image)

**Figure 14**

Anodic Current Density/Potential Curves on Copper Surface after Heat Treatment in Atmospheres containing Oxygen

Curve 1: without Heat Treatment
Curve 2: 1 hour at 100 °C
Curve 3: 2 hours at 100 °C
Curve 4: 4 hours at 100 °C

RE: Calomel (SCE) 241.5 mV/NHE; CE: Glassy Carbon; scan rate: 1 mV/s; T: 30 °C; 10 g/L KOH; N$_2$ purging; without agitation
Figure 15

Anodic Current Density/Potential Curves on Copper Surface after Heat Treatment in Atmospheres containing Oxygen

Curve 1: without Heat Treatment, after immersion in Na$_2$O$_8$S$_2$
Curve 2: 2 hours at 100 °C
Curve 3: 4 hours at 100 °C
Curve 4: 24 hours at 100 °C

RE: Calomel (SCE) 241.5 mV/NHE; CE: Glassy Carbon; scan rate: 1 mV/s;
T: 30 °C; 10 g/L KOH; N$_2$ purging; without agitation
Typical current density/potential curves on copper surfaces of bulk material in alkaline potassium hydroxide solution after heat treatment are shown in figure 14. Bare copper surfaces show first an increase of anodic current density until a maximum of the current is reached (curve 1: 108 μA/cm²). After this critical current (passive current density) a decrease of current is observed. In the range between 0 mV/SCE and +600 mV/SCE uncovered copper surfaces have an anodic current of about 7-9 μA/cm². When the copper surface is covered with copper-oxide (conditioned by heat treatment) the passive current density increases up to 1 mA/cm² (Curves 2, 3 and 4) and the anodic current decreases to 1-20 μA/cm². The fact that samples with and without heat treatment show almost the same behaviour is to be found in the fact that copper builds also oxides at room temperature.

Therefore a new series of experiments was carried out. All samples were first immersed in 50 g/l sodium persulfate solution (Na₂O₈S₂ + H₂SO₄ pH = 1) for 2 to 3 minutes to remove oxides from the surface. After this procedure the samples were exposed to a heat treatment at 100 °C in oxygen atmospheres several times. After this the effect on anodic behaviour in alkaline solution was much more marked (Fig. 15).

Copper without oxides (measured immediately after immersion in Na₂O₈S₂- solution) shows a peak of anodic current density of about 4 μA/cm² (curve 1). Such peaks increase with increasing time of heat treatment which means an increase of oxygen content on the copper surface (curve 2). After 4 hours the maximum of oxygen content is reached (curve 3). Heat treatment for more than 4 hours (24 hours) at 100 °C (curve 4) does not change the anodic potentiodynamic behaviour dramatically, but there is a difference of the open-circuit potential of samples after heat treatment for 4 hours and those which were exposed to 100 °C for 24 hours.
4.4.2 Potential versus Time Measurement

Open-circuit potentials increase with increasing time of heat treatment (Fig. 16). Samples without heat treatment have an open-circuit potential of about \(-250 \text{ mV/SCE}\), while samples after 24 hours have an open-circuit potential of about \(+25 \text{ mV}\) against a saturated calomel electrode. The difference in open circuit potential (sample become more noble versus heat treatment) means, oxide formation after 4 hours at 100 °C is not complete.

Figure 16
Open Circuit Potential versus Time Curves of Copper Surface after Heat Treatment in Atmosphères containing Oxygen

Curve 1: without Heat Treatment
Curve 2: 1 hour at 100 °C
Curve 3: 2 hours at 100 °C
Curve 4: 4 hours at 100 °C
Curve 5: 24 hours at 100 °C

RE: Calomel (SCE) 241.5 mV/NHE; T: 30 °C; 10 g/L KOH; N₂ purging; without agitation
4.4.3 Two-Electrode Measurement

More rapid, without extensive and expensive equipment, the same results, as sensitive as with electrochemical methods described above, could be obtained by using the two-electrode measurement technique. As shown in figure 17 and figure 18, the potential response of copper during galvanostatic measurement (15 μA/dm²) depends upon the state of oxygen content on the surface.

Differences in the final potential after 30 seconds could be explained with an in-homogeneous formation of copper oxide during heat treatment (curves show results of 5 measurements on the surface of one sample). In the case of different samples the same behaviour was found (not shown as a figure). The curves of different samples become more similar if time of heat treatment increase. Galvanostatic measurements therefore support the thesis that oxygen formation at 4 hours is not complete.

![Figure 17](image1.png)

Potential versus Time Measurement of Copper Surfaces before and after Heat Treatment: 100°C, 1 Hour

RE: Stainless Steel (CrNi18/8); Electrolyte: 1 % KOH; T: 25 °C; i<sub>anodic</sub> = 15 μA/dm²; without agitation and purging with N₂
Potential versus Time Measurement of Copper Surfaces after Immersion in Sodium Persulfate (Na₂O₈S₂) Solution and after Heat Treatment: 100°C, 4 and 24 Hours

RE: Stainless Steel (CrNi18/8); Electrolyte: 1% KOH; T: 25°C; i_anodic = 15 μA/dm²; without agitation and purging with N₂
4.5 Bronze (CuSn6) Substrates

To improve the electrochemical techniques described before, the three- and two-electrode measurement methods were tested under laboratory conditions with samples manufactured under production conditions. The aim of the experiments was to optimise a pretreatment process for electronic workpieces using efficient cleaning steps like alkaline immersion cleaning and electrolytical degreasing methods. Samples were pins for connectors (5 x 10 mm) made by copper-tin material (CuSn6) covered with different types of lubricants after several drawing procedures. Degree of cleanness required depends on the electrochemical deposition of tin afterwards.

As shown on the samples (Ag, Au and Cu) before, first of all typical current density/potential curves were made (Fig. 19).

Figure 19
Anodic Current Density/Potential Curves of Bare Copper-Tin Surfaces (CuSn6). Measurement on different Samples manufactured under Production Conditions

RS: Calomel (SCE) 241.5 mV/NHE; CE: Glassy Carbon; scan rate: 1 mV/s; T: 30 °C; 10 g/L KOH; N₂ purging; without agitation
Copper-tin alloys have the tendency to form oxide layers which are very hard to remove depending upon the content of tin. But as shown in figure 20 the current/density potential curves from copper-tin bulk material with 6% tin is more similar to copper than to tin in 1% KOH solution.

Figure 20
Anodic Current Density/Potential Curves on Copper, Tin and Copper-Tin Alloy (CuSn6)
RE: Calomel (SCE) 241,5 mV/NHE; CE: Glassy Carbon; scan rate: 1 mV/s; T: 30 °C; 10 g/L KOH; N2 purging; without agitation
If samples are covered with different kinds of lubricants, potentiodynamic measurements are difficult to explain because lubricants on a metal surface act as a resistor which allows only the measurement of very low current densities near the sensitivity of the potentiostat; the possibility of errors during measurement thus increases.

A very proved and more sensitive measurement method for this type of measurement problem is the electrochemical impedance measurement. As shown in figure 21 lubricants cause curves different to active surfaces (treatment in sodium persulfate) or oxidised copper tin surfaces during storage.

![Nyquist Diagram of Copper-Tin-Alloys covered with different Lubricants (RAZIOL FS 1S, WYNN'S FS 1S), activated in Na₂O₈S₂ Solution and covered with Oxides during Storage](image)

**Figure 21**

Nyquist Diagram of Copper-Tin-Alloys covered with different Lubricants (RAZIOL FS 1S, WYNN'S FS 1S), activated in Na₂O₈S₂ Solution and covered with Oxides during Storage

Curve 1: CuSn₆ covered with Lubricant RAZIOL FS 1S
Curve 2: CuSn₆ covered with Lubricant WYNN'S FS 1S
Curve 3: Without any Treatment (Oxides)
Curve 4: After Etching in Na₂O₈S₂ (60 s, RT)

RE: Calomel (SCE) 241.5 mV/NHE; CE: Glassy Carbon; T: 30 °C; 10 g/L KOH; Initial Frequency: 100 kHz; Final Frequency: 10 mHz; Ac Amplitude: 10 mV; N₂ purging; without agitation
Effect of Immersion Cleaning and Electrolytical Cleaning Processes on Impedance Response of Copper-Tin-Alloy covered with Lubricant (RAZIOL FS 1S)

Curves:
1. Without Cleaning (Covered with Raziol FS 1S)
2. After Etching in Na₂O₈S₂ Solution (60 sec, RT)
3. After Immersion Cleaning (60 °C, 5 s) and Electrolytical Cleaning (40 °C, 5 A/dm², 60 s)

RE: Calomel (SCE) 241.5 mV/NHE; CE: Glassy Carbon; T: 30 °C; 10 g/L KOH; Initial Frequency: 100 kHz; Final Frequency: 10 mHz; Ac Amplitude: 10 mV; N₂ purging; without agitation

Although this measurement method is very sensitive in detecting lubricants on the surface of copper-tin alloys electrochemical impedance measurements have the disadvantage that the measurement time per experiment (curve) takes from 30 minutes up to several hours (depending on the kind of coverage) and essential equipment is very expensive. Impedance measurement in this form in the moment is limited to fundamental investigations in laboratories. Therefore it was of great interest discovering the possibility of galvanostatic two-electrode methods to optimise pretreatment (cleaning) processes.
Effect of Different Lubricants on Voltage Response during Galvanostatic Measurement of Brass and Bronze Substrates after Anodic Immersion in 10 g/l KOH for 30 Seconds

I\text{anodic}: 15 \mu\text{A/dm}^2

RE: Stainless Steel (CrNi18/8); Electrolyte 1% KOH; Temperature: 25 °C; without agitation and purging with N\textsubscript{2}

The results in figure 23 show different influence on response potential depending on the type of lubricants. Highest resistivity is given by using RAZIOL CLF 25 E while Lubricant WYNN'S causes much more lower resistivity. Chemical analysis to justify this different behaviour were carried out but at present state of examination with little success. Further analyses perhaps with the opportunity to describe electron passage throughout lubricants will be useful.
For manufacturing limits good and bad degreasing conditions were limited by simple empirical tests like adhesion and corrosion tests on samples (brass and bronze) electroplated with ECD-tin. From this a limited voltage (0.2 V) corresponding to good degreasing conditions was found (Fig. 24).

![Graph showing potential vs. time for good and bad degreasing conditions.]

**Figure 24**

Good and Bad Degreasing Conditions for Pretreatment of Tin-Lead (CuSn6) Electrodeposition on Brass or Bronze in General
Figure 25
Pretreatment of Brass for Tin-Lead (CuSn6) Electrodeposition
Potential Response versus Different Degreasing Conditions for Different Lubricants from Punch Press
RE: Stainless Steel (CrNi18/8); Electrolyte 1% KOH; Temperature: 25 °C;
without agitation and purging with N₂
Figure 26

Pretreatment of Bronze for Tin-Lead (CuSn6) Electrodeposition Potential Response versus Different Cleaning Conditions for Different Lubricants from Punch Press

RE: Stainless Steel (CrNi18/8); Electrolyte 1% KOH; Temperature: 25 °C; without agitation and purging with N₂
Pretreatment of Brass and Bronze for Tin-Lead (CuSn6) Electrodeposition - Potential Response versus Different Cleaning Conditions for Different Lubricants from Punch Press

RE: Stainless Steel (CrNi18/8); Electrolyte: 1% KOH; Temperature: 25 °C; without agitation and purging with N₂
4.6 Steel Substrates

Steel is a very common substrate material for the electroplating industry. Because of the low corrosion resistance in most of atmospheres, if no special compounds like chromium, nickel or molybdenum are added (stainless steel), steel have to be protected from corrosion attack by either organic or inorganic (i.e. electroplated) coatings with more noble metals like copper, nickel, zinc, tin or chromium.

During storage or forming processes, both cutting and non-cutting processes, steel is normally covered with corrosion preventives and/or drawing compounds. Therefore for cleaning before electroplating to take place is essential.

When steel surfaces without any additional treatment (inorganic or organic coating) are used, the degree of cleanliness could also be important. The example given in figure 28 is a steel used in the computer manufacturing industry for pins. Because a fixed insertion force is demanded and because impurities on the steel surface increase insertion force, estimation of the degree of coverage after electrolytical degreasing procedure is important.

Figure 28

Adsorbed Drawing Compounds on Steel Surface determined by Scanning Electron Microscope (SIMS)

Steel: Sandvik 20 AP (1% C, 0.15% Si, 0.4% Mn, 0.02% P, 0.05% S, 0.2% Pb)
To improve the possibility of two-electrode measurement for assessing cleaning conditions on steel, pins were immersed in different cleaning solutions and afterwards examined both by the electrochemical measurement and Energy Dispersive X-Ray Microanalyser (EDX). For comparison a series of pins without any pretreatment were tested.

Cleaning Procedure I
according to ASTM G 1-90 [187]

- Solvent Cleaning
  Acetone, 30 s, RT

- Rinsing
  H₂O, 15 s, RT

- Alkaline Cleaning with
  Ultrasonic Support, 50°C, 180 s, Cleaner 1190, Schlotter, Germany

- Rinsing
  H₂O, 15 s, RT

- Rinsing
  Ethanol, 5 s, RT

- Drying
  air

Cleaning Procedure II

- Solvent Cleaning
  Acetone, 30 s, RT

- Rinsing
  H₂O, 15 s, RT

- Alkaline Cleaning with
  Ultrasonic Support, 50°C, 180 s, Cleaner 1190 Schlotter, Germany

- Rinsing
  H₂O, 15 s, RT

- Electrolytic Cleaning
  Cathodic: 5 A/dm², 40 °C, 30 s, Cleaner KG, Schlotter, Germany

- Rinsing
  Ethanol, 5 s, RT

- Drying
  air

Results are summarised in figure 29, 30 and 31. Solvent cleaning in addition with alkaline cleaning removes most of the typical impurities on the steel surface present under these production conditions, but an amount of Silicon is still very large (Fig. 29). Voltage Response of current density versus time measurement is appropriate in a range of 1.3 to 1.5 V. Practical tests show an insufficient state of cleanliness by a very high insertion force of the pins. In contrast to these phenomena are pins, which are additionally cleaned in an electrolytical cleaning solution (cathodically), having very low voltage response, a very low amount of silicon-impurities, and low insertion force. These examples show that the two-electrode measurement is a very quick, cheap and sensitive method to estimate impurities on metal surfaces including silicon, which is often a cause of bad adhesion of electrochemical deposited metals and alloys.
Adsorbed Impurities on Steel Surface without any Pretreatment determined by Energy Dispersive X-ray Microanalyser (EDX) and corresponding Galvanostatic Potential versus Time Measurement

RE: Stainless Steel; Electrolyte: 1% KOH; T: 25 °C; I anodic: 20 μA/dm²; without agitation and purging with Nitrogen
Steel: Sandvik 20 AP (1% C, 0.15% Si, 0.4% Mn, 0.02% P, 0.05% S, 0.2% Pb)
Adsorbed Impurities on Steel Surface after Solvent Cleaning and Alkaline Cleaning with Ultrasonic Support determined by Energy Dispersive X-ray Microanalyser (EDX) and corresponding Potential versus Time Measurement (Galvanostatic)

RE: Stainless Steel; Electrolyte: 1% KOH; T: 25 °C; I_anodic: 20 μA/dm²; without agitation and purging with Nitrogen
Steel: Sandvik 20 AP (1% C, 0.15% Si, 0.4% Mn, 0.02% P, 0.05% S, 0.2% Pb

Figure 30
In another experiment the two-electrode measurement method was compared with the acid copper test [107,108], a visual test method to estimate the degree of cleanliness on steel surfaces. For the acid copper test the workpieces must be made from a material electrochemically active in sulphuric acid solution in comparison with copper (i.e. iron). For the experiment samples were immersed in the following solution:

- 50 g/L Copper Sulphate, CuSO₄ * 5 H₂O
- 0.1 g/L Wetting Agent (CUDEC AN 030501, Schlotter, Germany)
- pH = 3 with Sulphuric Acid, H₂SO₄

On steel surface areas free from impurities copper will be deposited by chemical activity. The ratio of covered areas to uncovered areas (copper : steel) at a fixed exposure time, or the period of time until the whole area of the samples is covered describe degree of cleanliness. Figure 32 shows the surface of steel substrates in a bare state and covered with three types of oils before and after immersion in the acid copper solution described above. Exposure time depends on the moment when deposition of copper starts. On steel substrates without any oil copper deposition starts immediately after immersion in acid copper solution and the whole area is covered after 30 seconds. If the steel surface is oily it takes about 180 seconds in same solution until first copper deposition is observed.

![Figure 32](image)

**Figure 32**

Steel Surface after Immersion in Acid Copper Solution
The main problem of the acid copper sulphate test is the fact that it is a visual test method. First of all it is very difficult to observe the exact start of copper deposition, and to get equal conditions all over the whole surface of workpiece is a second problem. By adding a wetting agent into the test solution copper deposition becomes more homogeneous. In figure 33 typical forms of copper deposition versus exposure time are sketched. The single rectangles ought to show a typical shape of numerous of experiments. Evaluation of only a few (< 3) samples does not make sense, because results vary and single measurements are hardly comparable. Nevertheless the test shows an interesting tendency: Different types of oils show different behaviour in the acid test solution.

Electrochemical resistivity of oil TOWER E-103 is much more marked than i.e. electrochemical resistivity of oil RAZIOL-CLF 25 E. If steel substrates are covered with RAZIOL-CLF 25E copper deposition could be observed after 30 to 60 seconds immersion in copper solution even if now pretreatment process was carried out before. This means that either the oil-film is very porous, seen from the point of view of electron passage, or the oil is soluble in acid solution and therefore partly destroyed during the test.

As discussed above evaluation of results from the acid copper test is sometimes difficult. Galvanostatic two-electrode measurements in comparison are more explicit and at least as sensitive. Figure 34 shows the potential response of steel surface in bare state, covered with oil TOWER E-103, after pickling in hydrochloric acid and after different state of electrolytical and immersion degreasing. The potential of steel is very low after immersion in hydrochloric acid (0.2 - 0.3 V). In this state steel surface is very active. Potential increases in the course of time to a range of 0.4 - 0.55 V if workpieces are immersed to atmosphere (bare state). In contrast, potential response of a steel surface is very high if it is covered with oil (1.2 to 1.5 V). After electrolytical or immersion degreasing potential decreases continuously. In the course of cathodic electrolytical cleaning these effect is particularly marked. In contrast to this potential response of samples after anodic electrolytic cleaning is notable.
After anodic treatment of steel in alkaline solutions the potential response is almost the same as observed on steel without any pretreatment. It seems that two-electrode measurements could be able to give information about electrolytical hydrogen or oxygen evolution during cleaning procedures. Certainly more accurate results require more experiments to get clarity. Experiments with different oils (RAZIOL- FS 1S and RAZIOL- CLF 25E) on steel show the same results. But in contrast to the acid copper test galvanostatic measurement enables to show different behaviour of oils depending, on the kind of degreasing process, is more selective (Fig. 34). If samples were not exposed to any pretreatment process, potential is in the range of $1.2 - 1.5 \text{ V}$. After alkaline cleaning with and without ultrasonic support, potential decreases to a range not far from those measured on covered surfaces. This means it is hardly possible to remove these types of oils in an alkaline cleaning solution neither without nor with ultrasonic support. Increase of exposure time from 30 to 180 s also does not improve cleaning conditions. Only when the temperature of the solution is comparatively high (70 °C) and applied exposure time is about 180 s, may the potential partly decrease. But this state of cleanliness of the steel surface is inadequate for the following electroplating processes. The cleaning effect is more pronounced if steel, covered with drawing oils, is immersed in a cathodic electrolytical cleaning solution. However, the potential is still at values ($0.8 - 1.1 \text{ V}$) which indicates residues on the surface. When ultrasonic support and electrolytic cleaning are used together (Fig. 35) a surface free of residues is created and the potential response drops to values equal to those measured on bare steel ($0.4 - 0.6 \text{ V}$). In general these experiments show not only a certain value of potential response after a fixed measuring time (30 seconds), they also show typical variations on the shape of the curves. For example, if a surface is covered homogeneously with an oil or if the surface is in a bare state, measurement curves are straight. If the organic film is inhomogeneous or if on the surface there are still residues after a certain cleaning procedure, it takes up to 30 seconds until a fixed potential is reached.
<table>
<thead>
<tr>
<th>Cleaning Procedure</th>
<th>Steel Substrate Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare State</td>
<td>Steel Substrata covered with Oil</td>
</tr>
<tr>
<td>TOWER E-103</td>
<td>+ 30 s US</td>
</tr>
<tr>
<td></td>
<td>+ 30 s Cathodic</td>
</tr>
<tr>
<td>RAZIOL-FS 1 S</td>
<td>+ 30 s US</td>
</tr>
<tr>
<td></td>
<td>+ 30 s Cathodic</td>
</tr>
<tr>
<td>RAZIOL-CLF 25 E</td>
<td>+ 30 s US</td>
</tr>
<tr>
<td></td>
<td>+ 30 s Cathodic</td>
</tr>
</tbody>
</table>

**Immersion Acid Copper Test, Minutes**

US: Alkaline Cleaning with Ultrasonic Support, 50 °C, Cleaner 1190, Schötter, Germany
Cathodic: Alkaline Cathodic Electrolytic Cleaning, 40 °C, 5 A/dm², Cleaner KG, Schötter, Germany

Figure 33

Acid Copper Test on Steel before and after different Cleaning Procedures
Figure 34

Effect of different Cleaning Procedures on Potential versus Time Measurement on Steel Surface (Galvanostatic)

RE: Stainless Steel; Electrolyte: 1% KOH; T: 25 °C; \( i(\text{anodic}) = 20 \, \mu A/dm^2 \); without agitation and purging with nitrogen
Steel: Sandvik 20 AP (1% C, 0.15% Si, 0.4% Mn, 0.02% P, 0.05% S, 0.2% Pb)
After Alkaline Cleaning with Ultrasonic Support, 50 °C, 30 s

After Alkaline Cleaning with Ultrasonic Support, 50 °C, 30 s and
After Electrolytic Cleaning (Cathodic, \( i = 20 \, \text{A/dm}^2 \)), 40 °C, 30 s

Figure 35

Effect of different Cleaning Procedures on Potential versus Time Measurement on Steel Surface (Galvanostatic)

RE: Stainless Steel; Electrolyte: 1% KOH; \( T: 25 \, \text{°C} \); \( i(\text{anodic}) = 20 \, \mu\text{A/dm}^2 \); without agitation and purging with nitrogen
Steel: Sandvik 20 AP (1% C, 0.15% Si, 0.4% Mn, 0.02% P, 0.05% S, 0.2% Pb)
5. Discussion

5.1 Experiments with different Metal Substrates and different Kind of Coverage

The experiments carried out have the aim of investigating the possibility for assessing cleaning conditions for metal surfaces using electrochemical methods. The main methods used are primarily concerned with the electrochemical polarisation characteristics of metal surfaces in different state of cleaning. In comparison with decontaminated metal surfaces, contaminated metal surfaces show a different electrochemical behaviour. Therefore, a measurement cell was developed which is on the one hand easy to use, rapid and economical and on the other hand able to give reproducible results.

First of all, experiments carried out were designed in this way that the principle possibility of the new measurement method, with respect to the grade of accuracy and detectability, could be demonstrated. Criteria for sample selection were the different types of substrates (metals), soils (organic and inorganic) and finally the degree of cleanness required by the different applications of workpieces.

Additionally samples were examined by other electrochemical measurement methods (potentiodynamic polarisation, impedance, etc.), by physical measurement methods, like scanning electron microscope (SIMS), electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy (AES) and finally by simple qualitative test methods, like the acid copper test to estimate the grade of cleanliness in comparison.

Silver and gold, both as electroplated coatings as well as bulk materials have a high selectivity towards sulphur. Covered with n-alkylthiols (CH₃–CH₂)ₙ–CH₂–SH silver and gold allow the study of structure and boundary phenomena of organic coatings on metal surfaces and within the physical organic chemistry of interfaces.[188-190] From there this kind of coating or impurity (in case of very low concentrations) is an excellent system to test the new measurement method.
Anodic current density curves of uncovered silver show typical shapes depending on the kind of solution. While silver in potassium cyanide solution is soluble (linear increase of anodic current versus potential) immersion in potassium hydroxide solution generates typical maxima according to the formation of Ag$_2$O$_2$ and AgO. Both in sodium-sulphate or in sodium-chloride solution this phenomena will not be observed. If silver is covered by $n$-alkylthiols the appearance of oxidation-peaks is suppressed. Because this already occurs after adsorption of the first monolayer of thiols it is a very sensitive marker.

Gold uncovered with organic films like $n$-alkylthiols do not generate maxima in current density responses as found on silver surfaces, because of the different electrochemical reactions of the two of them in alkaline solution. Nevertheless there is a dramatic difference between potential response for gold coated with $n$-alkylthiol and of bare gold surface, which makes detection of this kind of organic impurity possible.

Potentiodynamic measurement requires appropriate equipment and certain time for preparation and carrying out the experiments. Both should not be the aim of the new electrochemical measurement method. Therefore a small cell was designed which allows the "galvanostatic polarisation" of metal with two-electrode technique. Easy to use, rapid (measuring time: 30-60 seconds) and cost effective are the advantages of the cell at first. But a high sensitivity and high reproducibility of the results are just as important.

Therefore numerous experiments with $n$-alkylthiols with different carbon-chain length, further organic materials, like lubricants, fatty grease, human sweat, India rubber, etc. and inorganic coatings, like chromate layers were carried out. To sum up it can be said that all these materials, regardless of whether they are bound by physical absorption or chemisorption, can be detected by this electrochemical method. It could be shown that in the case of $n$-alkylthiols on silver and gold this simple electrochemical measurement cell could
be as sensitive and precise as physical measurement methods, like SIMS, ESCA and AES are. In contrast to these analytical methods this type of galvanostatic measurement allows a description of the state of a metal surface immediately after pretreatment without any extra preparation. Description of the grade of cleanliness with a high grade of accuracy after different solvent cleaning procedures (at RT and at boiling point of solvent) is also possible.

As indicated above, gold and silver have a high selectivity towards sulphur. Especially on silver surfaces it is very hard to remove n-alkylthiols completely. For most of applications the degree of cleanliness required does not mean the total removal of every thiol, because further treatment is even possible. Therefore two-electrode measurement in practical use at a production line must not be able to detect the last thiol molecule on a surface.

But similar results estimated both by AES and galvanostatic measurement after vacuum treatment of covered silver show how sensitive such galvanostatic measurements could be. To receive a silver surface totally free from thiol require vacuum treatment for 7 days at 120 °C. Only after this extreme treatment sulphur or sulphur compounds are no longer detected by Auger electron spectroscopy. Easier and with comparable sensitivity two-electrode measurement comes to the same results. Only if all thiol is removed a characteristic potential for uncovered silver is measured. The disadvantage that polarisation measurement could not detect the identity chemical compounds containing sulphur, if some is detected on the surface, is an advantage in this special case, because n-alkylthiols cause a typical increase of the potential, as many other organic films do. Other sulphur compounds, i.e. detected as Ag₂S on a silver surface after a corrosion attack, react as an inorganic coating comparable with oxide layers. Therefore, there is no need to select the real sulphur compound from numerous of signals.

Because of this, very selective electrochemical behaviour of the n-alkylthiols on gold and silver these substances could be detected unmistakably and, with the aid of the differences
in electrochemical response, without any lavish instrumental analysis. To improve the possibility of detection of oxides with electrochemical measurements, copper as a bulk material was investigated. Typical curves on copper surface after immersion in sodium persulfate solution (copper surface free of oxides) and after heat treatment in atmospheres containing oxygen for varying time at 100 °C were therefore carried out. Copper oxides cause a higher anodic current and an increase of the current maxima of potential/current density curves at passivation potential.

It seems that in alkaline solution (pH > 12) the formation of copper reactants (Cu₂O, CuO, Cu(OH)₂) generates a barrier layer for electrons closer than those produced during heat treatment in atmosphere containing oxygen (Cu₂O and CuO). If copper surfaces with and without artificial oxide-layers are polarised anodically, the formation of a thick barrier layer for samples with oxide-layers, created by previous heat treatment, is not possible as copper samples without previous heat treatment can form. From there a higher anodic current in the corresponding potential range results. The range where passivation of copper occurs was found to be from +240 to +750 mV/NHE in 1 % KOH solution.

Potentiodynamic polarisation on brass substrates (CuZn) do not show a similar effect. Passivation current decreases when exposure time of heat treatment at 100 °C increases (1-24 h). This means that either oxide formation on brass during heat treatment or the formation of corrosion products during polarisation in KOH is different from pure copper.

While open potential versus time measurement, potentiodynamic current density/potential measurements and galvanostatic two-electrode measurements give significant current or potential response, thickness of copper oxide-layers on the one hand is sometimes too thin for any estimation with for example glow discharge optical spectroscopy (GDOS) or on the other hand only a qualitative determination of oxides is possible. In contrast to this, it is possible to measure the amount of copper(I)oxide and copper(II)oxide on copper for wire bonding.
and on lead-frames quantitatively with electrochemical measurements as some authors reported [191].

Impurities, like lubricants from drawing procedures on copper and copper alloys cause a typical electrochemical "finger print". Lubricants can be identified all the time on the lower anodic current density in the passive region and/or on current maxima at passivation potential. Amount of current density is different, depending on the kind of material (Cu, CuZn or CuSn6), but always typical for the single metal. The finger print allows one to find out the best cleaning conditions for copper, brass and bronze due to following electrodeposition (i.e. tin).

Sometimes lubricants act like a resistor so powerful that sensitivity limits of the potentiostat during potential/current measurement are reached. Potentiodynamic techniques must then be replaced by an electrochemical impedance measurement. As shown on bronze (CuSn6) Nyquist diagrams yield curves with significant differences depending not only on the state of the surface (bare or oxides) but also on the type of lubricant. Although impedance measurement is very sensitive in detecting organic compounds on metal surface this technique has disadvantages. Measurement time per experiment takes from 30 minutes up to several hours and essential equipment is very expensive. If the aim of the investigation is not reasoned in the study of the chemical and electrochemical reactions, galvanostatic two-electrode measurement could be an useful tool, instead of the impedance measurement because it is a cheap and rapid method. The received results show that not only detection of coverage by lubricants is possible, this technique is also able to measure differences depending on the kind of lubricants - at least in the case of the four lubricants investigated.

But the main aim of the investigations was to show that in principle it is possible to optimise a process technique (pretreatment and electrodeposition) with the help of galvanostatic measurement. Therefore, different pretreatment processes were carried out and their suitability was evaluated
by the two-electrode measurement. As a result an optimised production process for tin deposition on brass or bronze substrates was created in a short time.

The third group of typical substrates investigated were steel and stainless steel. In the case of steel, one series of experiments was carried out on steel covered with drawing compounds. Another series was executed for the purpose of comparing galvanostatic measurements with a simple, well known test method for cleanliness of iron: the acid copper test.

Steel could be covered with drawing compounds containing the element silicon probably as silicate or silicone, which cause a lot of trouble to following processes. The results of two-electrode measurement were compared with energy dispersive X-ray microanalyses (EDX). Both techniques allow the estimate the effectiveness of i.e. solvent cleaning, alkaline cleaning, either with ultrasonic support or cathodic electrolytic cleaning, using commercial solutions. Cleaning conditions can be optimised by two-electrode technique even if data of chemical compounds could not be obtained with this technique.

In comparison with the acid copper test evaluation of results is much easier using galvanostatic measurement. Its cause is to be found in the fact that the acid copper test is a visual test, influenced by many parameters of the experiment itself, like temperature, age of test solution, time, number of samples, etc. Therefore a lot of experience is necessary to distinguish nearly similar coverages, often received after acid copper test. In contrast to this, results of galvanostatic measurement are in form of potential values, relative separate, in principle practicable for further adaptation by computer (with more expensive equipment) and at least more sensitive.

During the experiments with stainless steel in a bare state and when covered with lubricants a special problem was observed. Stainless steel builds passive layer on atmosphere and during anodic polarisation in alkaline solution (1% KOH). Current density/potential curves therefore do not always result in significant effects. It seems that both reactions,
passivation and response from the organic coverage (lubricants act as a resistor), produce U/I curves, which look alike in the sum of their electrochemical reactions. Only at values more noble (cathodic) than 1 - 1.2 V/NHE distinct differences were obtained. This is a potential range where oxygen evolution occurs. Current response of covered surface is lower than those from bare steel surface. An impeding of the creation of oxygen bubbles, which were in a equilibrium with oxygen development at the anode (workpiece) could be the reason why response current is lower.

Nevertheless during galvanostatic measurement differences between surfaces being either passive or covered can be measured. At this stage of investigations it is not totally understandable why this discrepancy between potentiodynamic and galvanostatic measurement exists. To give a thorough explanation more experiments must be carried out.

5.2 Design of Cell

Design of a cell must consider distinct requirements caused by electrochemical regularity as well as from considerations concerning a greatest practicability. Because the cell should be of small size and easy to handle, a little container made from plexi-glass was used similar to those manufactured for coulometric measurements (Fig 36). The transparent material has a good resistance against most of the chemicals at moderate temperatures and enables one to identify changes of the electrolyte or within the arrangement of working/counter electrode.

Only a relatively small amount of test solution was required for the size of the cell, but could cause problems. During anodic experiments a perfect test solution should be very large compared with the amount of soluble substances. Only in this case influence from this substances to the electrochemistry can be neglected. Experiments presented were therefore done in that way so that every experiment was carried out with a new test solution and exposure time was as short as possible. For principle studies this could be a practicable method. But for applications in a production line or a labo-
Figure 36
Design of Cell for Two-Electrodes Measurement Methods and Potentiodynamic Three-Electrodes Measurement Methods
ratory for quality control, more conveniences and a more rapid measurement method is necessary. Therefore, a further model should be used which enables complete change of the test solution in a short time by pumping the solution in and out of the cell. Measurements beyond room temperature will then also easily be possible.

Potassium hydroxide (1 % KOH) as an electrolyte, in contrast to acid solutions, was found out to be suitable for most of metals, because dissolution does not occur or is so low that results are not influenced significantly by this kind of reaction. Additionally most of the cleaning solutions, except solvent cleaning and pickling, are neutral or alkaline solutions; applications directly in a cleaning media will be easier. Since the cell is totally covered, electrolyte could not flow out because of tiny decompression. If the hole at the bottom of the cell is not too large (Ø 1.5 mm), therefore no diaphragm is necessary where troublesome ions could be concentrated.

Influence on the measurements caused by the arrangement of counter electrode to working electrode is not as critical. An optimal position of the counter electrode is 5 mm from the hole straight-line to the working electrode (sample).

As a counter electrode a cylinder (Ø 6 mm x 40 mm) made of stainless steel was used. Stainless steel under these conditions has a stable free open-potential and can be installed like a reference electrode. Nevertheless experiments with an additional reference electrode were carried out in this way, that a tube was applied (size and material equal those described above) instead of the solid cylinder. A plastic pipe filled with saturated KCl-solution and agar-agar acts as an electrolyte-bridge. At one end of the pipe (inside the cell) a glassy diaphragm was fixed, while at the other end (outside of the cell) a small tank was installed. In this reservoir a reference electrode (SCE) could be inserted.
5.3 Further Investigations

Although this type of cell, as presented, is best for the task described above, yet some limitations in view of modified measurement methods exist. Therefore for further investigations some suggestions may be recommended. The probability to assess many localised positions on one sample because of design of cell and basically of the small size of measurement area needed is at first an advantage. But measurements directly in an cleaning solution will be practicable only if design of cell is modified. This could involve an extra Haber-Luggin capillary, which makes potential measurements or measurements of current flow over longer distances possible, or at least a different cell and technique must be used.

First experiments show that the corrosion current caused by different free open-potentials of counter- and working electrode could be used to classify the degree of cleanliness. The new cell could be a type corresponding to the principle of the evaluation of conductivity in electrolytes. An important requirement is a fixed distance between counter- and working electrode. Counter electrode could be either a stainless steel (act as a reference electrode) or an electrode made from the same material as the workpieces consist.

If the material of both of the electrodes is exactly the same, potential differences and resulting corrosion currents could only be caused from different reactions at the interface of the electrodes. In actual practice this state could be reached when the counter electrode is cleaned perfectly before an experiment starts. Under these conditions a coverage with soil, oxides, etc. on the surface of working electrode creates a potential difference between the two electrodes, corresponding to the degree of coverage on the workpiece. If then soil or impurities are recovered, the electrochemical active area on the surface, equal to the counter electrode, increases and potential difference decreases. As a result the current (corrosion current) flow between counter electrode and working electrode is less.
While an extra Haber-Luggin capillary in principle will not change the basic experiments carried out, experimental limits of the new cell must be determined again. Influence of the additives in cleaning solution and cleaning conditions (temperature, cathodic or anodic current, ultrasonic support, etc.) could be expected. Nevertheless first experiments were carried out, which showed that an application in principle is possible. After calibration in an appropriate cleaning solution and after perfect cleaning of the counter electrode, cleaning process of the workpiece could be observed in-situ. (Fig. 37). A main disadvantage of this technique is the fact that preparation of a good standard counter electrode is a problem and ratio of anode : cathode is not uncomplicated. Therefore more experiments must be carried out.

Not only do the results received verify this simple measurement method to be able for an assessment of surface cleanliness for metal surfaces, it could offer in addition a possibility to study fundamental aspects of cleaning processes. Therefore, another aim for further studies could be the investigation of cleaning reactions (reactions at the interface on a metal surface) using this methods. Results from this work show that an association of pure research work done in laboratories and a simple test method, developed primarily to construct an element for a production line, using more or less sensitive, comfortable or sophisticated electrochemical measurement methods, could be possible.
Typical Current / Time Curves

Basic Circuit Diagramm

Figure 37
Two-Electrode Measurement Method (Current Measurement) to Estimate Cleaning Process in-situ
6. Conclusions

Before plating processes occur pretreatment of the substrate is essential. Any selected cleaning media as well as any preferred cleaning conditions must depend on the substrate, the quality and amount of soils and contaminants to be removed and on the degree of cleanliness required. In the case of electroplating processes perfect cleaning is very important, since the adhesion and numerous properties (i.e. porosity, structure, etc.) of the deposited metal or alloy depend upon the efficiency of cleaning. An appropriate selection of compatible cleaning procedures first requires measurement methods to estimate the degree of cleanliness. Therefore several methods of cleanliness measurement exist.

Simple methods of determining the degree of cleanness of metal surface like water-break test, acid copper test, atomiser test or very sensitive methods, like AES, SIMS, ESCA etc. show many disadvantages. Some of them are very inaccurate, while others are actually sensitive but very complicated to use. Therefore often a combination of different methods is required in order to get a complete picture of different types of contamination and state of treating. Indication of a momentary status of the surface is common to them all, because measurement during treatment is impossible.

This project has been instituted to investigate the possibility for assessing cleaning conditions for metal surfaces using electrochemical methods. It has been primarily concerned with the electrochemical polarisation characteristics of metal in different state of cleaning. In comparison with de-contaminated metal surfaces, contaminated metal surfaces show a very different electrochemical behaviour.

In order to be of direct use to the production line a desirable measurement method requires a combination of characteristics. It must be easy to use without specialist competence, reliable enough to give reproducible results and at the same time rapid and cost effective. Investigations for development of a simple electrochemical measurement cell on the principles of galvanostatic technique must also consider this.
In a first step the aim has been to improve sensitivity and reproducibility of this type of measurement cell for metal surfaces after cleaning procedures. Silver and gold surfaces covered with n-alkylthiol therefore are excellent systems because of their high selectivity towards sulphur. Different state of coverages could be estimated including the effect of very small concentrations of impurities. Theoretically single alkylthiols could be detected.

Electrochemical behaviour of oxide layers and the influence of metals, which are able to create a passive layer, like stainless steel do, on the correctness of the measurement method was investigated too. Results from galvanostatic measurements were compared with other electrochemical and analytical methods and qualitative test methods, like the acid copper test on iron. Finally, to improve measurement technique under production conditions, a pretreatment process for brass and bronze substrates for electroplating with tin was carried out.

To sum up all the results received and all the experience made during this work, it can be pointed out, that galvanostatic measurement with this cell is very sensitive and accurate.

The aim of the work to develop and test a measurement method which is easy to use without specialist competence, reliable enough to give reproducible results and at the same time rapid and cost effective, was fulfilled; at least for the examples shown before.

Certainly interpretation of the results is sometimes difficult, if no or very slight information of the process or the reactions occurring at the interface is available. But this is a general problem of electrochemical measurement methods, because always a summarised potential or current is measured. Nevertheless galvanostatic two-electrode measurement could be an usable tool for the assessment of surface cleanliness for metal surfaces.
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