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Development of Water-soluble Systems for Use in Industrial Soldering Processes

Abstract: This communication discusses the engineering considerations involved in the design of low-polluting water-soluble systems for use in mechanized soldering processes. New formulations for water-soluble fluxes, lubricants, and solder masks are described and test data are presented.

Introduction

In recent years society and government have intensified their concern about the increased amounts of industrial waste that are entering the environment [1]. In response to this concern, a number of manufacturing firms have undertaken studies to find ways of reducing or eliminating noxious effluents from their plants while at the same time controlling production costs and maintaining production rates at levels that will satisfy growing consumer demands for their products.

This communication reports a development project intended, in part, to reduce pollution in one important area of electronics manufacturing—the soldering process. Three elements of the soldering process were subjects of the development effort: fluxes, lubricants, and masking materials. Although water-soluble fluxes, lubricants and solder masks have been available for some years, none of them known to the authors were totally satisfactory for the specific combination of machine and product characteristics to which the materials would be applied.

The development project resulted in the invention of some new materials that have been successfully introduced to the manufacturing line. However, the main purpose of this communication is to discuss the engineering considerations involved in the design of water-soluble materials for use in industrial soldering machines. These discussions are intended to be helpful in the design of similar materials tailored to various application situations.

Water-soluble fluxes

The functional properties required of any flux material can be categorized as follows:

1. The flux must be capable of removing organic dirt, grime, and metal oxides from the surface to be soldered.
2. The flux must permit the cleaned surface to be soldered at high temperatures and, at the same time, prevent air contact and subsequent oxidation of the heated surface.
3. The flux must be capable of easy removal from the soldered surface and any flux residue left from incomplete cleaning must be noncorrosive and nonconductive.

These requirements are well satisfied by the conventionally used rosin-based flux [2]. Rosin is a mixture of complex organic acids (see Ref. 3 for its constituents), which is solid at room temperature and melts at soldering temperatures (450 to 550 °F). The usual method of applying the rosin flux is in a "vehicle" such as an isopropyl alcohol solution or some other solvent having a low boiling point. Amine halides or hydrohalides are also part of the flux mixture as "activators" that serve to remove heavy concentrations of metal oxides and contaminants from the surface to be soldered. Because the rosin-based flux constituents are not water-soluble, they are usually removed from the soldered parts with chlorinated solvents. These solvents are used because they are capable of dissolving flux residues while remaining nonflammable at solder-process temperatures. Unfortunately, these solvents have low toxic limits (see Ref. 4). Furthermore, carelessness in the use of these solvents can result in fatal accidents [5].

It was determined that one particular wave-soldering operation consumed 100 gallons of trichloroethylene each production day. Engineering efforts to reduce the amount of solvent were intense, yet conditions of the manufacturing process and machinery precluded significant reduction of this consumption rate. Development of a water-soluble flux would allow manufacturing engineers to remove the halogenated solvents from the soldering process and, at the same time, replace those more costly solvents with water.

A suitable alternative to the rosin-based flux would necessarily have the three basic functional properties listed above. Since no single water-soluble material was known to have all those properties, experiments were conducted to determine satisfactory combinations of water-soluble materials. A variety of flux systems containing various proportions of the following types of constituents were tested.

1. Water-soluble organic acids to act as the "flux."
2. Amine hydrohalides to provide the necessary "activation."
3. Polyols to provide the anti-oxidation blanket.
4. Solvents to serve as diluents for the three constituents above.

Some of the formulations tested are shown in Table 1 and the observed effects are discussed in the subsequent paragraphs. Formulation 1 was found to have excessive "flux" and "activator." This was evidenced by the degradation of an electroless tin plating previously placed on the product to enhance wetting of the solder. The problem is illustrated in Fig. 1, where a ring of degraded tin is visible encircling the test solder. This formulation can lead to corrosion of electrical components and connector leads in the soldered product [6].

Formulations 2 and 3 are variations of the first formula, with low-boiling-temperature solvents added to act as diluents. These mixtures were no more successful than the first since, as the solvents evaporated, the concentrations of the flux and activator increased to the level at which corrosive attack on the electroless tin occurred.

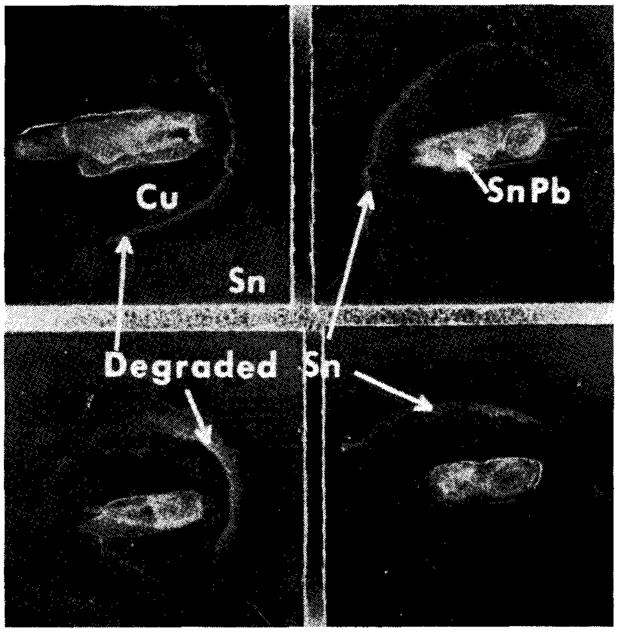

Figure 1 Degradation effects on soldered product resulting from flux formulation containing excessive "flux" and "activator."

It was evident at this point that the basic formulation would require lower percentages of activator and flux, and that it was necessary to include low-boiling solvents in the system to thin the mixture and improve its ease of application to the surface of the part to be soldered. Formulations 4 and 5, in which the total percentages of flux and activator were 1.5 and 2.0, respectively, were tested next. As expected, the concentrations of flux and activator increased as the solvents evaporated, and the solvents were effective in reducing the viscosity of the mixture. In this case, however, the flux-activator concentration was too low. The result was the formation of solder "spurs" (Fig. 2) on component leads that had been coated

Table 1 Various formulations of a water-soluble flux.

	Component percent by weight						
	Formulation Number						
Component	1	2	3	4	5	6	7
Methanol	–	–	40	35	30	30	24
2-propanol	–	–	–	–	14	17	12
2-butoxyethanol	–	25	–	18	14	13	14
Polyethylene glycol 200	86	65	51	45.5	40	36	44
Tartaric acid (flux)	11.5	8	7.5	–	1	3.3	5.2
Dimethylamine Hydrochloride (activator)	2.5	2	1.5	1.5	1	0.7	0.8

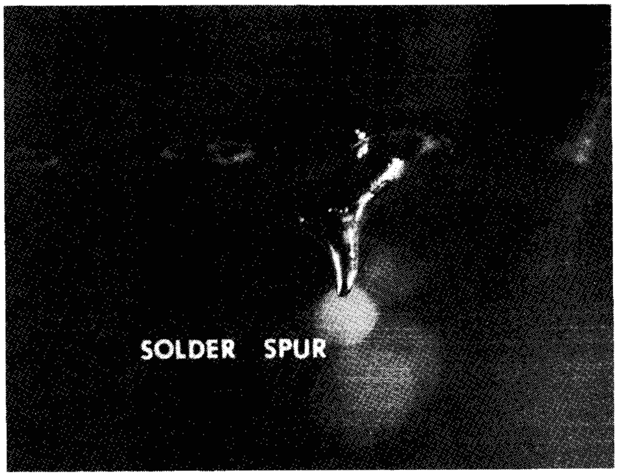

Figure 2 Solder spur formed on component lead as a result of using flux formulation containing too little "flux" and "activator."

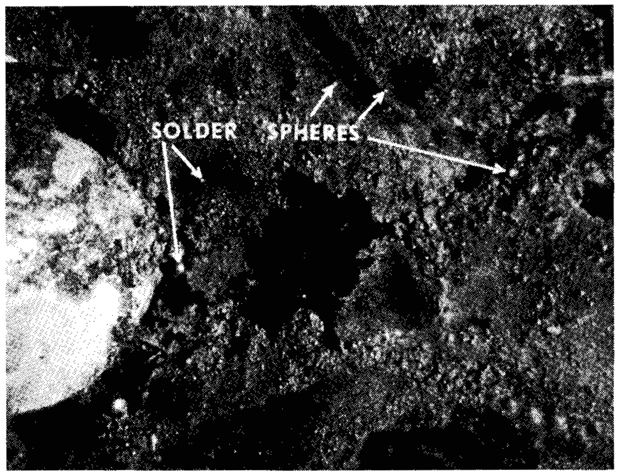

Figure 3 Solder spheres on surface of product resulting from explosion of residual solvent vapor during soldering process.

with 10/90 solder prior to the application of flux. This phenomenon occurs because the amount of flux and activator is too small to completely remove the high-melting-point 10/90 coating during the soldering operation. Because the partially plastic alloy rapidly cools to below its soldification temperature as the soldered product emerges from the solder wave, a spur is formed. Solidification temperatures of 10/90 and other high-lead alloys are significantly higher than the normal range of solder temperatures. The conclusion is that the flux system must contain a sufficiently high amount of flux and activator to assist the solder wave in eroding the high-lead alloy from the part being soldered.

Experience with the systems discussed above led to the blending of Formulation 6, which was used in a production environment for a period of time. It was found, however, that this formulation still had one minor defect. The relatively large amount of solvent used to lower the viscosity of the mixture resulted in the formation of solder spheres. A flux system containing low-boiling solvents must be devoid of these solvents when the fluxed part encounters the solder wave. Should residual solvent remain in the flux, rapidly expanding solvent vapor explodes, causing solder spheres to form. Usually, one can avoid this problem by preheating the part to be soldered immediately after the flux has been applied in order to assure that the solvent has fully evaporated prior to soldering. However, the particular wave-solder machine used when Formulation 6 was being tested did not permit preheat temperatures to be raised high enough to evaporate all the solvent. Hence, explosions of residual solvent vapor occurred, and solder spheres were formed on the surface of a soldered part as shown in Fig. 3. Although small-diameter spheres are of no great significance, spheres whose diameters are larger than 0.01 in. can lodge under components and between leads, causing electrical short circuits.

Formulation 7 [7] proved to be the mixture that was satisfactory in all respects for the intended application. The amount of solvent was small enough to be completely evaporated before vapor explosions could take place; the amount of flux and activator was large enough to prevent the formation of spurs and small enough to avoid corrosive effects. In terms of the motivation for the development process, the new formula provided a flux system that would permit halogenated solvents to be removed from the soldering process.

It is important to note, however, that the particular formulation discussed above is not universally applicable to all soldering processes. Flux constituents that work well on one product or solder machine will not necessarily perform adequately on another machine even with a similar product. The reason for this situation is that variations in machine characteristics, such as flux evaporation rates, preheat profiles, and machine speeds, affect the required flux composition. This makes it necessary for the engineer to tailor the flux to the specific characteristics of the machines and products he is working with.

Some flux materials that may be chosen to fit particular soldering situations are tartaric acid, urea, triethanolomine, oxalic acid, and malic acid. Some alternative activators are diethylamine hydrochloride, glutamic acid, 3° butylamine hydrochloride, ammonium chloride, and methylamine hydrobromide. There are also various low-boiling alcohols and cellosolves commercially available for use as solvents, and a variety of polyols and glycols available to provide the desired amount of viscosity.

Water-soluble lubricants

Chain drives in the wave solder machines and cleaning tanks were being lubricated with petroleum-based lubricants. These lubricants were occasionally dispersed in the rinse water and thereafter entered the plant waste outfall. In addition, it was found that the lubricant sometimes adhered to the soldered product, thus requiring further cleaning. This cleaning had to be accomplished with halogenated solvents or degreasers, which were also required for the periodic cleaning of the aged lubricants on the chain drives.

The conventional method of solubilizing high-molecular-weight petroleum lubricants has been to replace the hydrocarbons with oxyalkanes such as polyoxyethylene. Many such water-soluble lubricants have been commercially available for years. Introduction of the oxygen atom into the CH_2 chain produces sufficient polarity in the molecular structure to make it water soluble. However, the synthesis steps required to impart water solubility tend to increase the cost of the lubricant. To offset this cost increase, it was decided to dilute the lubricants with water and include surface-active agents and anti-corrosion agents to improve the functional properties of the lubricant.

Pin insertion tests were performed on various dilutions of the proposed lubricants to establish the reduction in frictional resistance these lubricants could provide. Petroleum-based lubricants were used as controls. Typical results of these tests are given in Table 2.

Tests on the contact resistance of the water soluble lubricant and dilutions thereof were performed on the pin contacts of several circuit cards. Electrical resistance values were compared with those obtained from a control sample of unlubricated cards. The data obtained indicate that no significant differences in average resistance values existed between the control sample and the samples lubricated with the water soluble lubricant or aqueous dilutions of it.

Table 2 Results of pin insertion tests.

Type of lubricant	*Average value of insertion force in pounds*[a]		
	Minimum	*Maximum*	*Average*
Petroleum oil	10.0	12.2	11.0
Water-soluble lubricant (WSL)	8.2	10.6	9.5
WSL – 50% H_2O	9.0	12.8	11.6
WSL – 30% H_2O	9.0	12.0	11.3

[a]The average value of the insertion force is based on a sample of at least eight card insertions.

Table 3 Components of water-soluble solder mask.

Component	*Functional property*	*Percent by weight*
Sodium Silicate	Basic solder mask component	50–60
Water	Diluent; reduce cost and viscosity	25–45
Rhodamine B Extra S[a] (red dye)	Visual inspection aid	0.05–0.1
Fluorocarbon	Anti-corrosion agent	0.03–0.3
Glycerol	Dispersing agent	5–15

[a]Product of the General Analine and Film Corp.

Water-soluble solder masks

With the incorporation of water-soluble fluxes and lubricants into the manufacturing process, soldering operations and subsequent cleaning operations became essentially pollution free. However, the use of a mechanical solder mask still presented a potential pollution problem in that pieces of masking material could enter the process effluent as solid waste. This becomes a significant problem as the industry is not permitted by government guidelines [8] to have any floating solids in its waste waters.

The solder mask mentioned above has commonly been a strip of thermally stable plastic tape placed over circuit card "through holes" which are not to be filled with solder. This operation is performed when it is desired to place special electrical components on the card after wave soldering. Although this tape acts as an excellent barrier to solder filling of the holes, it often presents a cleanup problem later in the manufacturing process. Spent tape has been found to stick to solder machine parts and to plug cleaning filters in the machine. Tape that does not become detached from the card must be hand picked from the card surface, a costly process.

Several commercially available solder masks were tested for possible use; however, many were found inadequate for the process as they were either water insoluble or would leave large amounts of residue. As a result, it became necessary to design a solder mask which would perform its intended function and meet the following criteria as well: 1) be water soluble, 2) leave little or no residue, and 3) present a low pollution potential.

A system based on sodium silicate was selected to meet these criteria. Sodium silicate or "water glass" has long been known to the industry. Used alone, however, it fails as a solder mask because it readily produces large amounts of residues which become difficult to clean with water. To offset this and other problems, a mask was designed of the materials given in Table 3.

Of those materials listed in the Table, perhaps the least obvious is the dispersing agent, glycerol. It was found that a small amount of glycerol in the mask de-

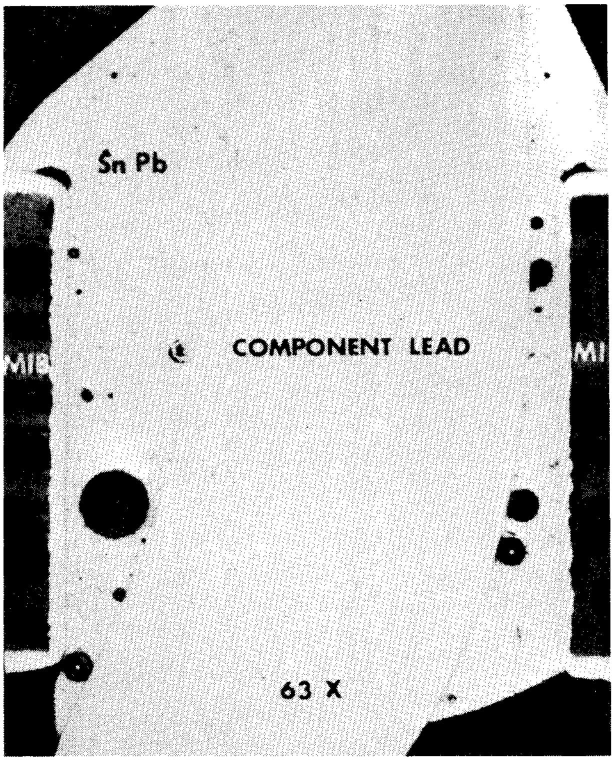

Figure 4 Cross section of soldered component lead examined to determine whether water-soluble mask had any adverse effects on hole filling and land wetting.

Table 4 Test results comparing functional ability of two water-soluble masks.

Drying time in hours	*Relative mask thickness*	*Percent of holes plugged* Silicate mask	*Percent of holes plugged* Organic mask
3	normal	0	5
3	excessive	0	24
72	normal	0	9
72	excessive	0	8
140	normal	0	–
650	normal	0	–

creased the amount of mask residue after the soldering operation. The reason for this is that the glycerol forms a solution with the mask and becomes trapped within its matrix as the applied mask hardens. After soldering, the glycerol is rapidly dissolved out of the mask in the cleaning tanks. As a result, the remaining mask is porous, providing an increased surface area, which allows the water in the cleaning operation to remove the mask in a shorter period of time. The same dispersing agent has an added benefit; glycerol readily absorbs water from the atmosphere. Therefore, any product which had been masked would tend to harden or dry out, but the presence of the glycerol would counteract this tendency and keep the applied mask in a pliable state up to several weeks after its application. This latter point is significant in that it is mandatory that the masked product not dry out and lose its effectiveness in the event that a machine breakdown prevents immediate soldering.

The designed mask system was then subjected to three important tests: functionality, solderability, and quality assurance. To be certain that the mask prevented soldering of designated through holes, a test of solder plugging was performed. Test data are shown in Table 4, where the silicate-based mask is compared to a second water-soluble mask composed of organic materials.

Note that the organic mask resulted in increased hole plugging (mask failure) as it was made thicker and allowed to dry longer. This was not the case for the silicate mask, even after prolonged drying.

To test the water-soluble silicate mask for solderability, several soldered leads were cross-sectioned and examined metallurgically. In every case, 100% hole fill was achieved and good wetting of the land area was observed. Occasional problems of poor solder wetting were overcome by using a slightly activated flux. A typical cross-sectioned joint is shown in Fig. 4.

The test for quality assurance was achieved by determining the insulation resistance of masked cards over prolonged periods of time. Typical test data for several analyses are presented in Table 5. The failure or "reject"

Table 5 Tests of insulation resistance as function of time after application of mask.

Card number	*Insulation resistance in megohms* — *Elapsed time, in hours, after application of mask*: 0	1	75	100	200	400
1	2.8×10^6	1.7×10^5	2.6×10^5	–	1.6×10^5	1.0×10^5
2	4.0×10^6	3.3×10^5	3.0×10^5	–	1.5×10^5	1.1×10^5
3	3.9×10^5	3.5×10^5	2.0×10^5	–	1.4×10^5	6.5×10^4
4	1.3×10^5	1.4×10^5	–	2.4×10^4	–	–
5	1.0×10^5	1.3×10^5	–	1.0×10^4	–	–
6	5.5×10^4	8.0×10^4	–	2.0×10^4	–	–
7[a]	1.0×10^6	9.0×10^4	3.8×10^5	–	1.5×10^4	9.5×10^3

[a]Control card masked with plastic tape.

resistance value for this particular test was 500 MΩ after 48 hours at 90°F and 85% relative humidity.

Replacement of the plastic tape operation by the water-soluble mask saved the manufacturing departments over 99% of the cost incurred using the tape mask. Furthermore, costs per unit hour dropped by as much as 50% in the application of the newer mask system. In addition, periodic shutdown of the cleaning machines for the purpose of removing tape was no longer necessary.

In summary, through the development and use of water-soluble systems, it has become feasible to remove many noxious solvents and other solid materials from the wave solder processes. The introduction of these water-soluble compounds reduced the costs of the process and allowed the savings accrued to offset the initial costs of phasing in the water soluble materials. Thereafter, products were manufactured at lower unit cost, and a significant step toward achieving a cleaner environment was realized.

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