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USE OF SURFACTANTS ADDED TO REFRACTORY SLURRY IN PRECISION FOUNDRY AND INVESTMENT CASTINGS WITH ALUMINUM

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ABSTRACT

The investment casting process, involving wax models invested with clays to give ceramic moulds from which metal castings are made is characterized by the obtainment of parts of high metallurgic quality , especially as far as dimensional aspects, complexity of design and surface finishings are concerned. The high precision parts have a wide application in the electronics, aeronautical, biomedical, textile and food industries. Twenty one different surfactants, added to refractive zirconite slurry, were tested for their efficiency in obtaining wetting and adherence to the surface of the wax and good quality finished aluminum parts. Only five surfactants, including sodium dodecylbenzene sulfonate, sulfonic acid, dioctyl sodium sulfosuccinate and ethoxylated long chain alcohols gave satisfactory results. Analysis of the specimens manufactured from 98% aluminum, poured at 710ºC, by visual observation, rugosity, optical photography and electron microscopy showed that they were of high quality. The present paper describes the results obtained with sulfonic acid C_{8-16} *and sodium dodecyl benzene sulfonate and explains the effect of the surfactants by the formation of a monolayer film or hemi-micelles between the wax and the ceramic slurry.*

RESUMO

O processo de fundição de precisão é caracterizado pela obtenção de peças de alta qualidade metalúrgica , principalmente sob o aspecto dimensional e acabamento superficial. Ele consiste da preparação de modelos de cera e de moldes cerâmicos e vazamento do metal fundido dentro dos moldes. A aplicação de peças microfundidas de alta precisão abrange muitas áreas , incluindo a indústria aeronáutica, eletrônica, alimentícia, textil e biomédica. Foram testados vinte e um surfatantes usando lama refratária contendo zirconita com respeito a sua eficiência à molhabilidade e aderência à superfície da cera e a obtenção de peças de alumínio de boa qualidade. Somente cinco surfatantes, incluindo ácido sulfônico, dioctil sulfosuccinato de sódio, dodecilbenzeno sulfonato de sódio e alcoóis etoxilados deram resultados satisfatórios. A qualidade alta dos corpos de prova, fabricados de alumínio com pureza de 98% vazado a 710ºC, foi comprovada usando métodos de análise visual, medidas de rugosidade, fotografia ótica e microscopia eletrônica. Este trabalho descreve os resultados obtidos com ácido sulfônico C_{8-16} *e dodecil benzeno sulfonato de sódio e explica o efeito dos agentes tenso-ativos através da formação de uma película (monocamada) ou hemimicelas entre a cera e a lama refratária.*

KEYWORDS: Investment Casting, Ceramic Slurry, Surfactants, Hemi-Micelles, Sulfonic Acid, Sodium Dodecylbenzene Sulfonate

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INTRODUCTION

The investment casting process is characterized by the obtainment of parts of high metallurgic quality, especially as far as dimensional aspects, complexity of design and surface finishing are concerned. The high precision parts have a wide range of applications including the aeronautical, electronics, biomedical, textile and food industries.[1-4] The value of the investment casting lies essentially in its ability to reproduce complexity of design and to achieve the tolerance necessary to eliminate difficult or impossible machining operations.[5-10]

Pure beeswax or common waxes modified with resins and fats have been used since ancient times in Europe, Asia and Africa to make models that were invested with clays to give ceramic moulds from which metal castings, especially bronze, were made. High quality art objects were manufactured in Italy during the 16th century, but the lost-wax process only became of modern industrial importance with the development of dental metallurgy and particulary the advent of the turbine engine in the years preceeding World War II.[5]

The manufacturing of high precision parts involves the following steps:

- Making of the wax model, as true as possible to the original part
- Fabrication of the ceramic mould using refractory zirconite slurry [6-9]
- Removal of the wax and baking of the ceramic mould
- Melting of the metal or alloy and metal casting (pouring of the melt into the mould) and
- Cleaning of the finished parts.

The refractory slurry usually contains zirconite or zirconium silicate ($ZrSiO_4$), traces of iron and titanium oxide and coloidal silica. An experimental problem that often arises is in obtaining adequate wetting and adherence of the clay to the surface of the wax.

Twenty one different surfactants, added to refractive zirconite slurry, were tested for their efficiency in obtaining good wetting and adherence to the surface of the wax and high quality finished aluminum parts. The surfactants tested were the following: sulfonic acid C_{8-16}, ethoxylated decyl alcohol (3 OE), sodium dioctyl sulfosuccinate, ethoxylated lauryl alcohol (4 OE), sodium dodecylbenzene sulfonate, hexadecyl trimethylammonium chloride, lead oleate; 3,7,11,15-tetramethyl-hexaden-1-ol; modified alkylphenyl polyglycol, ethoxylated castor oil (40 OE), ethoxylated lauryl alcohol (10 OE), nonyl-phenyl ether phosphoric acid, ethoxylated oleic acid (5 OE), triethanolamine dodecyl sulfonate, calcium dodecylbenzene sulfonate, dilauryldimethylammonium bromide, didodecyl phosphon-amide, ethoxylated lauryl alcohol (2 OE), organophosphonic acid and a dispersant with non-surfactant resins. Of these, only the first five gave good experimental results.

Analysis of the specimens or test parts manufactured from 98% aluminum, poured at 710ºC, was done by visual observation, rugosity, optical photography and electron microscopy.

The present paper describes the experimental results obtained with sulfonic acid C_{8-16} and sodium dodecylbenzene sulfonate added to refractive zirconite slurry.

MATERIALS AND METHODS

MATERIALS. The surfactants used were obtained from Chem Service Inc., West Chester, Pennsylvania, USA; Aldrich Chemical Company, Milwaukee, Wisconsin, USA; Henkel Produtos Químicos, Porto Alegre, RS, Brasil or Sarmisegetusa Research Group, Santa Fe, New Mexico, USA. They were used without further purification.

The wax employed is of common use in metal foundries in Brazil and consists of 23,00% paraffin; 53,00% tar; 10,67% Carnaúba wax (palm leaf wax); 12,00% mineral wax and 1,33% EVA (ethylene vinyl acetate).

The material used for the preparation of the refractory slurry or clay, called Zirconite ALM (empirical formula $ZrSiO_4$), was obtained from Nuclemon, São Paulo, Brazil. It has a melting point of 1540-1680ºC and consists of approximately 65% zirconia (ZrO_2); 33% silica (SiO_2); 0,05% ferric oxide (Fe_2O_3) and 0,10% titania (TiO_2).

The aluminum employed was industrial grade aluminum rods (98% purity).

MICELLE FORMATION. The critical micellar concentration (CMC) of the surfactants in water was determined at 25º, 32º and 40ºC by surface tensiometry using a Fisher Model 21 Semi-Automatic Tensiometer. The thermodynamic parameters for micellization, including the free energy, ΔG^{o}_{m}, enthalpy, ΔH^{o}_{m} and entropy of micellization, ΔS^{o}_{m}, were calculated using standard equations.[10-12]

TEST FOR WETTING. The wetting ability of the surfactants was tested by adding approximately 0,03% by volume of the surfactant to the ceramic slurry of density 2,81 g/cm^3, previously prepared. The mixture was stirred for 30 minutes and the wetting of the wax was tested visually. The concentration that gave total wetting was compared to the critical micellar concentration (CMC) in water.

PREPARATION AND PROPERTIES OF REFRACTORY SLURRIES. The refractory slurries or clays used in investment casting are usually classified into primary and secondary. The primary slurry contains particles of smaller size and is the subject of the present study. The secondary slurry contains particles of larger size (200 Mesh) and a lower density. They are both prepared in similar manners. The primary slurries or clays were prepared under controlled conditions (22 to 24ºC and 50% relative humidity) from 4 kg of zirconium silicate (270 Mesh) in 1 liter of ligand (colloidal silica) with mechanical stirring (30 rpm). Subsequently, the refractory slurries were allowed to rest for 24 hours in closed containers in order to prevent evaporation.

The present paper describes the refractory slurries 0 (no surfactant), 1 (containing 0,01% by volume of sulfonic acid C_{8-16}) and 4 (containing 0,03% by volume of sodium dodecylbenzene sulfonate. The aging process of the refractory slurries was studied over a period of five days by measuring the following properties:

- Viscosity (using a Zahn cup Nº 5 at 22ºC)
- Density (using a 10 ml volumetric flask and an analytical balance
- pH (using indicator paper)
- Capacity of Coverage (determination of quantity of dry clay that adhered to a glass plate of known area immersed in the slurry.

WAX MODELS. The models used had U shape and dimensions of 20 x 20 x100 mm. The wax employed has been described above.

CERAMIC MOULDS. The ceramic moulds were prepared by two alternate immersions of the wax model in the primary slurry and refractory stucco (foundry zirconite, 100 Mesh), followed by four layers of secondary slurry and showering with larger particles containing silicon and aluminum oxides with diameters of 0,5 to 2 mm.The time needed for drying after each immersion bath varied from 2 hours for the first two layers up to 5 hours between the fifth and the sixth layer. The drying was allowed to take place naturally at 22ºC and a relative humidity of 50% . The preparation of the secondary slurry is similar to the primary one, the main difference being the larger granulometry of the zirconite ($ZrSiO_4$), approximately 200 Mesh.

DE-WAXING AND CALCINATION. The removal of the wax (de-waxing) and calcination were done in an autoclave at 900ºc. The procedure usually required 1-2 hours and was usually performed after the covering with the last layer.

MANUFACTURE AND ANALYSIS OF THE ALUMINUM PARTS. Molten aluminum of 98% purity was poured into the ceramic moulds at 710ºC soon after their removal from the autoclave. As soon as the metal solidified, the mould was broken and removed and the surface of the manufactured part was cleaned.Analysis of the finished aluminum parts was then done by visual observation, measurement of rugosity, optical photography and electron microscopy. The castings test specimens were designated CP-0 (ceramic slurry without surfactant), CP-1 (with sulfonic acid C_{8-16}) and CP-4 (slurry containing sodium dodecylbenzene sulfonate.

RESULTS AND DISCUSSION

The thermodynamic parameters determined for the micellization of sulfonic acid C_{8-16} and sodium dodecylbenzene sulfonate in water at 25ºC are summarized in Table I. The sulfonic acid sample, obtained from Henkel Produtos Químicos,contained alkyl chain lenghts that varied from eight to sixteen carbon atoms.

TABLE I. THERMODYNAMIC PROPERTIES FOR THE FORMATION OF MICELLES OF SULFONIC ACID C_{8-16} (SA) AND SODIUM DODECYLBENZENE SULFONATE (SDBS) IN WATER AT 25ºC.

Surfactant	Critical Micellar Concentration (mole/l)	ΔG^{o}_{m} (kcal/mole)	ΔH^{o}_{m} (kcal/mole)	ΔS^{o}_{m} (eu)
SA	$1,81\times10^{-4}$	-5,10	-1,65	+11,6
SDBS	$1,05\times10^{-3}$	-4,04	+2,70	-22,6

Both surfactants, from the same supplier, were used without further purification. The experimental results obtained for the critical micellar concentration (CMC) and the standard free energy of micellization (ΔG^{o}_{m}) are typical for surfactnts in aqueous solutions.

Figure 1 illustrates the variation of properties such as flow viscosity, surface coverage and density as a function of concentration of zirconite determined for primary slurry without surfactant at 22ºC. The density and the coating or surface

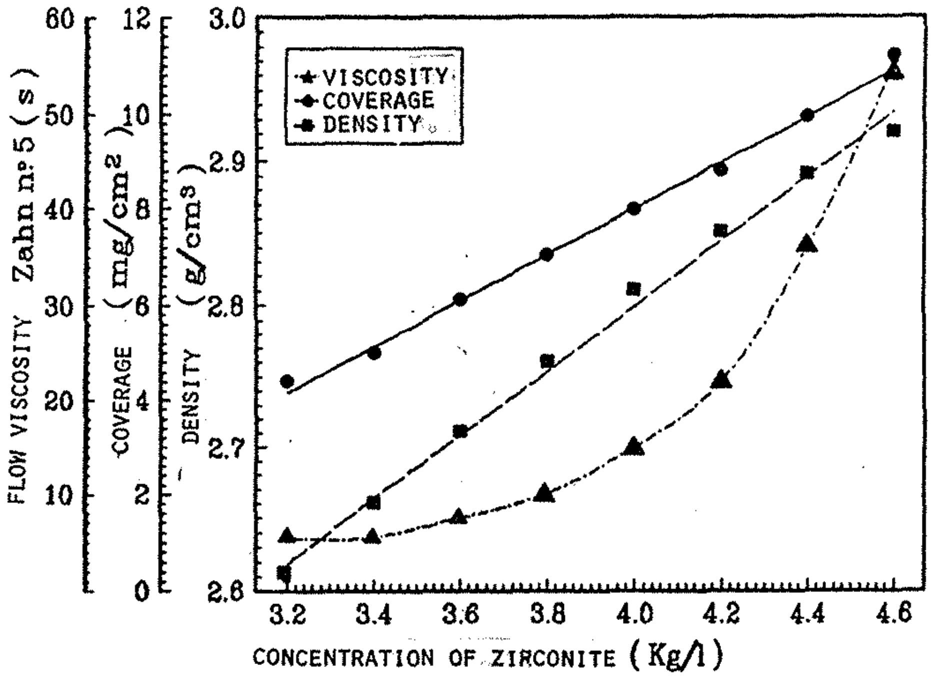

FIGURE 1. VARIATION OF SOME PROPERTIES OF PRIMARY CERAMIC SLURRIES WITHOUT SURFACTANT AS A FUNCTION OF THE CONCENTRATION OF ZIRCONITE AT 22ºC.

coverage varied linearly as a function of the content of zirconite, while the flow vsucosity exhibited an exponential behavior. All the studies described in the present paper were done with slurries of fixed density (2,80 g/cm^3).

Figures 2 and 3 show the variation of the density and flow viscosity of ceramic slurries without surfactant(slurry 0) and in the presence of the two surfactants, sulfonic acid C_{8-16} (SA- 0,01% by volume, slurry 1) and sodium dodecylbenzene sulfonate (SDBS-0,03% by volume, slurry 4) as a function of time.

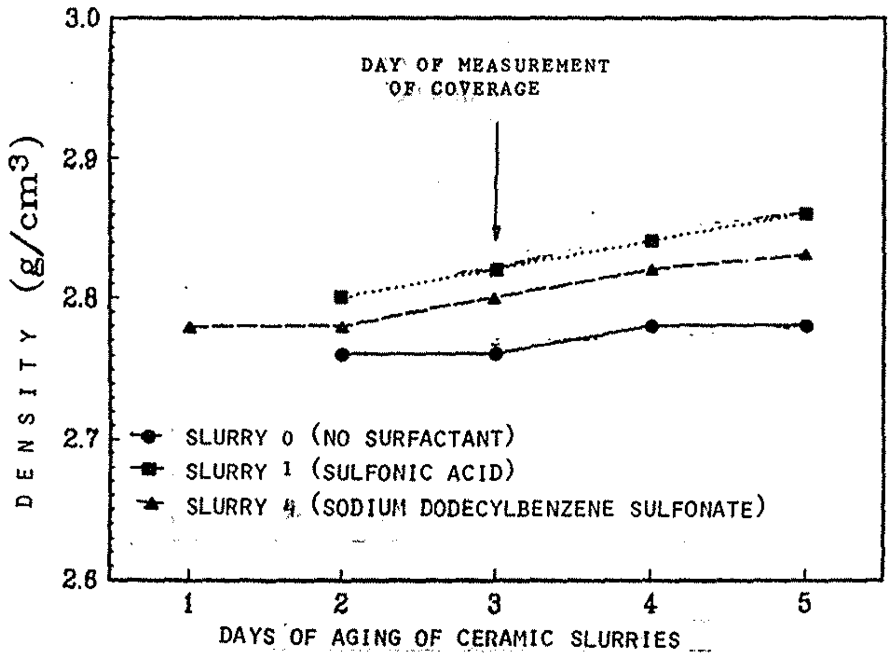

FIGURE 2. EFFECT OF AGING ON THE DENSITY OF CERAMIC SLURRIES IN THE PRESENCE AND ABSENCE OS SURFACTANTS AT 22ºC.

The effect of aging is much more pronounced for the slurries containing surfactants. The surface coverage, determined on the third day by the dipping slide method, showed no significant difference. The corresponding experimental values for the same density (2,80 g/cm^3) were 7,97g/cm^2 (slurry 0); 7,93 g/cm^2 (slurry 1) and 7,60 g/cm^2 (slurry 4), respectively.

Of the twenty one different surfactants added to refractory slurry, only five gave satisfactory wetting and adherence between the clay and the wax model. They were sulfonic acid C_{8-16}, sodium dodecylbenzene sulfonate, sodium dioctyl sulfosuccinate y ethoxylated decyl alcohol (3OE) and ethoxylated lauryl alcohol (4OE). In general, the wetting ability depends to a large extent on the affinity of the hydrophilic parts of the surfactants for the ceramic clay and the chain length of the surfactants.

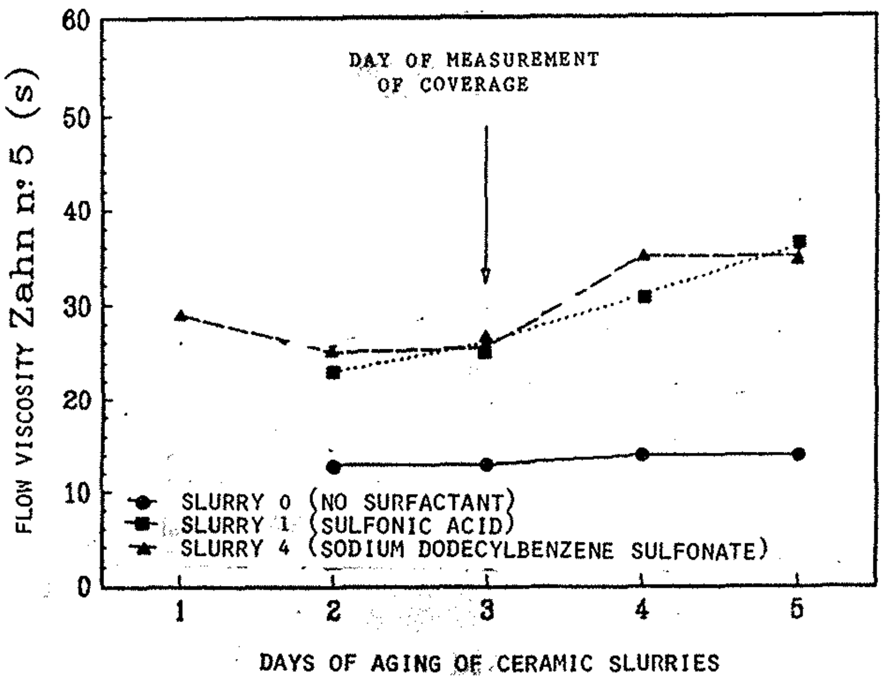

FIGURE 3. EFFECT OF AGING ON THE FLOW VISCOSITY OF CERAMIC SLURRIES IN THE PRESENCE AND ABSENCE OF SURFACTANTS AT 22ºC.

Anionic surfactants such as sulfonic acid C_{8-16} (SA), sodium dodecylbenzene sulfonate (SDBS) and sodium dioctyl sulfosuccinate appear to meet these criteria. For the ethoxylated long chain alcohols, the presence of the oxygen atoms (part of the ethoxy group) and a ceratin critical chain length seem to be important.

The wetting with sodium dodecylbenzene sulfonate occurs at a concentration of 8,73 x 10^{-4}M, that is below the CMC in water. For sulfonic acid C_{8-16} the concentration (3,65 x 10^{-4}M) needed for satisfactory wetting and adherence is above the CMC. For cases of surfactant present in concentrations below the critical micellar concentration (CMC), one model that can be proposed is the formation of a monolayer film between the wax and the ceramic clay. This may be the case of sodium dodecylbenzene sulfonate (SDBS) with the polar head groups in contact with the ceramic slurry and the hydrophobic tails in the proximity of the wax (Figure 4).

For experimental conditions where the concentration of surfactant is slightly above the CMC (as with sulfonic acid-C_{8-16}) the formation of hemi-micelles may be suggested. This is illustrated in Figure 5.

Both kind of aggregates have been described in the literature for various solid-solution interfaces, including silica-water.[13-16]

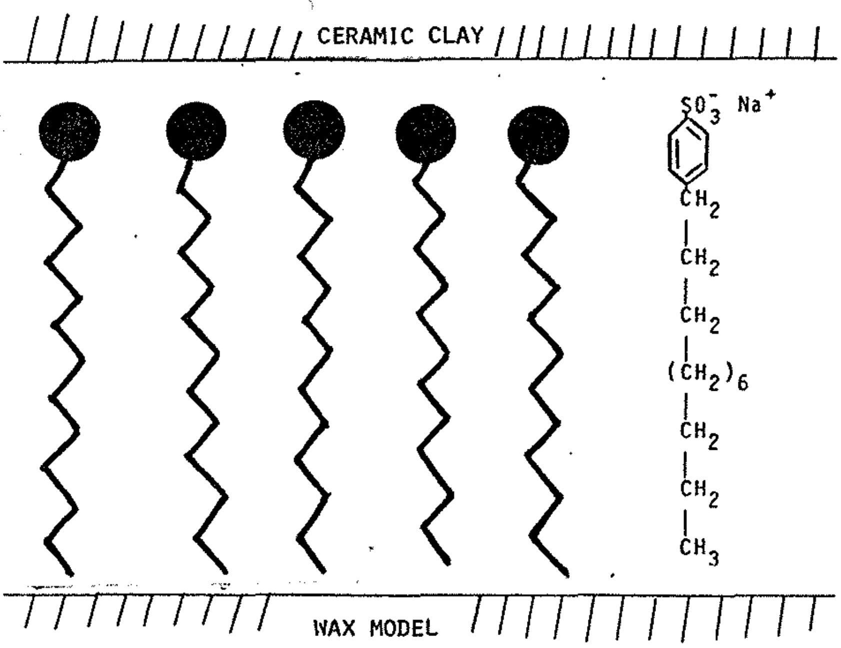

FIGURE 4. DIAGRAM OF THE ORIENTATION OF THE SURFCATANT MONOLAYER FILM BETWEEN THE WAX MODEL AND THE CERAMIC CLAY.

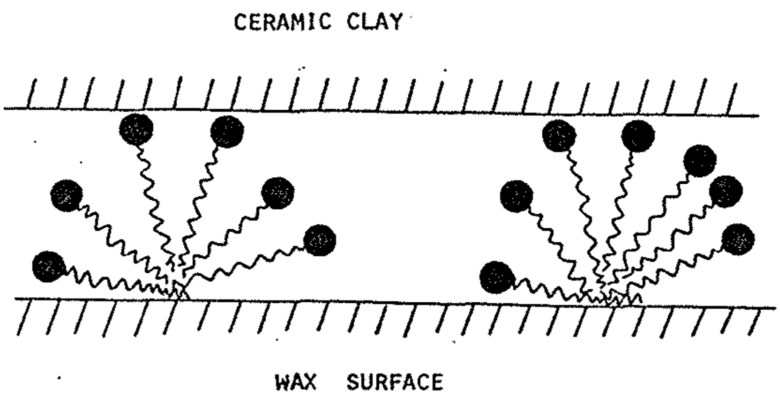

FIGURE 5. DIAGRAM ILLUSTRATING THE FORMATION OF HEMI-MICELLES BETWEEN THE WAX MODEL AND THE CERAMIC SLURRY.

The nature of intermolecular forces and the stability of colloids are rather complex subjects and no attempt will be made to discuss them here. They have been described in detail in the literature.[17,18]

Refractory slurries represent theoretically stable systems since they contain colloidal dispersions with refractory materials and surfactants. Refractory slurries tend to gel when repulsive interactions have been sufficeintly reduced and the Van der Waals attractive forces begin to predominate. London forces are also important in such systems, since apolar molecules may be subject to polarization due to fluctuation of charges in other molecules. At the refractory clay-wax interface London, Van der Waals and Landau forces may be limited due to the presence of surface tension. This appears to be the case for the wetting and adherence of a refractory slurry on the surface of the wax in the presence of surface active agents.

Figure 6 shows optical micrographs (magnification factor 11x) of smooth and rough reference surfaces and also finished aluminum castings specimens obtained with ceramic slurries wihout surfactant (CP-0), containing sulfonic acid C_{8-16} (CP-1) and sodium dodecylbenzene sulfonate (CP-4).

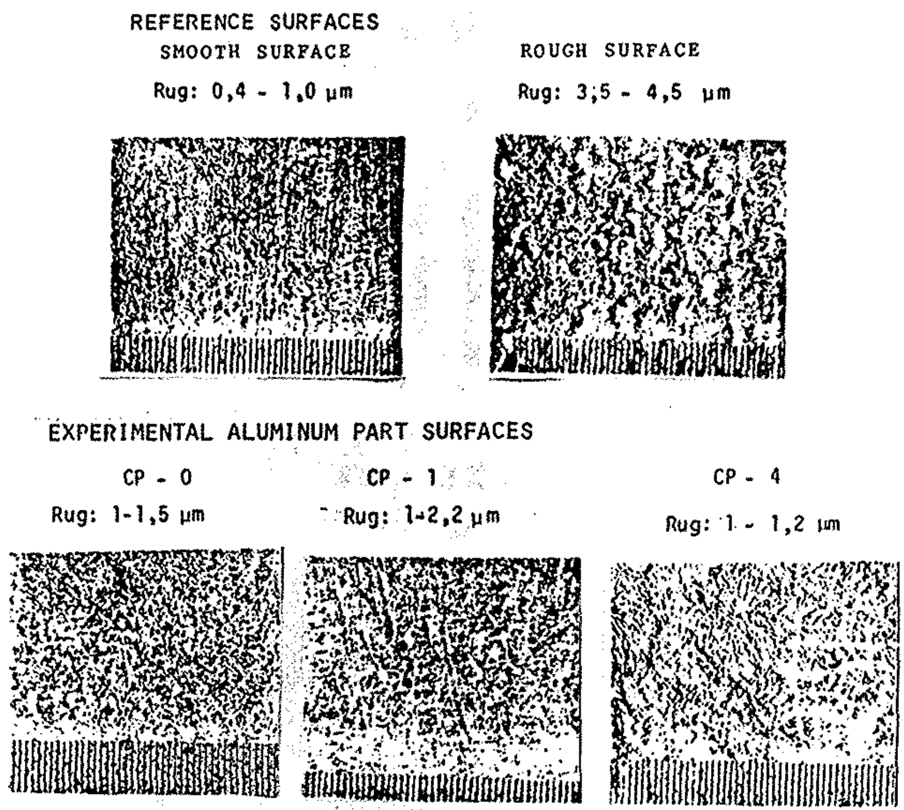

FIGURE 6. OPTICAL MICROGRAPHS OF ALUMINUM CASTINGS SPECIMENS AND THEIR RESPECTIVE RUGOSITY. (CP-0, no surfactant; CP-1, with sulfonic acid C_{8-16}; CP-4, with sodium dodecylbenzene sulfonate).MAGNIFICATION 11X.

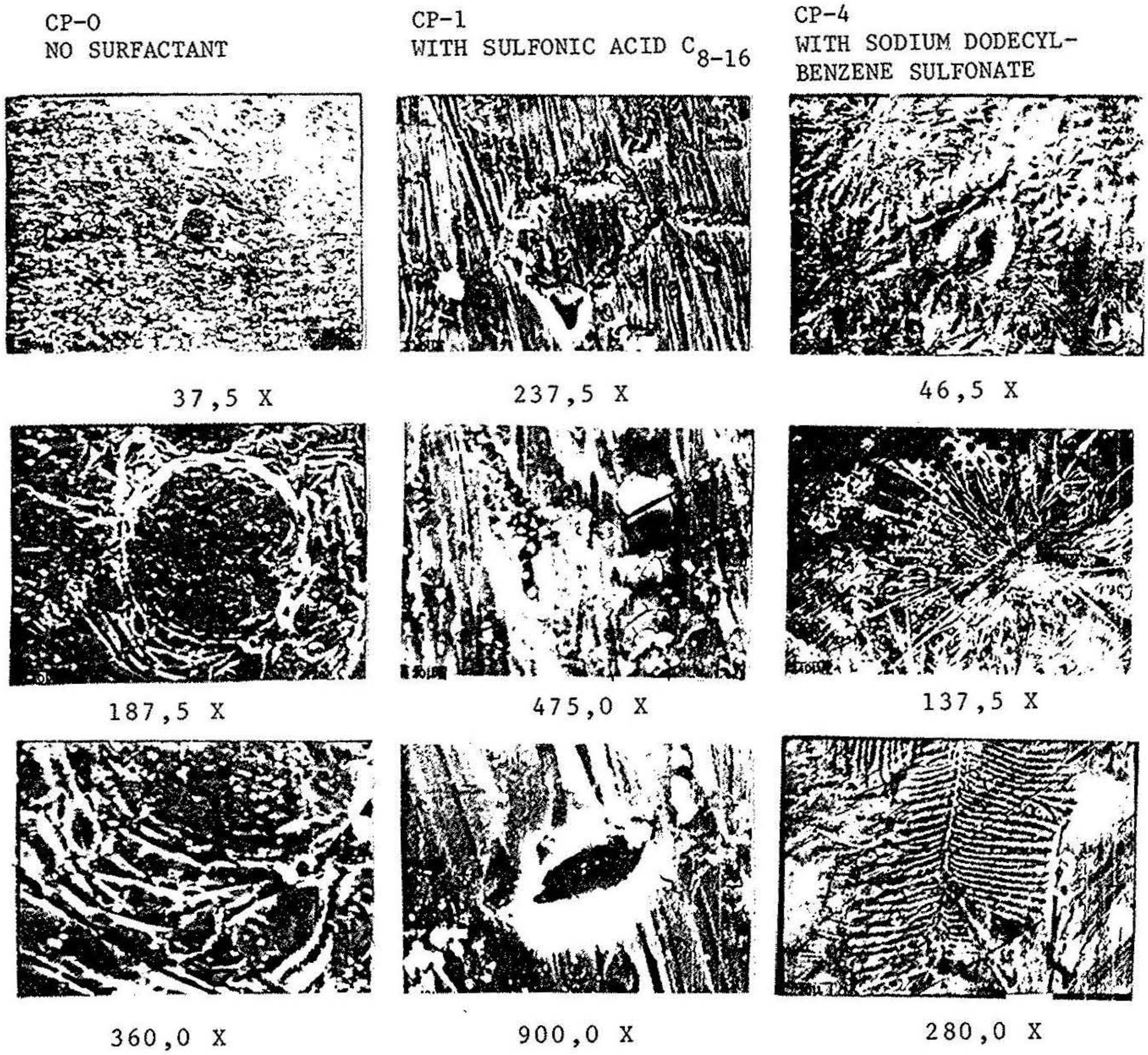

FIGURE 7. SCANNING ELECTRON MICROGRAPHS OF ALUMINUM CASTINGS SPECIMENS.

In general, the optical micrographs show good surface finishing for the aluminum parts.

Figure 7 illustrates some representative scanning electron micrographs of the aluminum castings specimens manufactured in this study. All micrographs show inclusion of refractory material on the surface of the metal, formation of microcavities and an oxide layer. The sequence of micrographs with increasing magnification for CP-O probably illustrates the formation of a cold drop and a series of ondulations on the surface caused by the variation of temperature during solidification. The sequences for CP-1 and CP-4 show the formation of oxides,among other phenomena.

Rugosity (Ra) may be defined as the average deviation of absolute values of the effective profile ordinates with respect to a median line across a length of sampling.

$$Ra = 1/L \int_0^L |Y|\, dx \quad \text{or} \quad Ra = 1/n \sum^n |Y|$$

The determination of rugosity was done with a Mitutoyo Rugosimeter, Model Surftest III. A sensor needle measured the rugosity of the surface in micrometers (μm). It usually scanned a length of 17 mm of test surface at a speed of 2 millimeters per second. The minimum sample length used for measuring the rugosity was 0,80 mm. The average values were obtained by measuring three different castings specimens within each group (CP-0, CP-1 and CP-4).

Figure 8 shows the variation of rugosity in terms of the Brazilian Norm, the average rugosity of the finished parts and the rugosity of the pattern used in this study. The Brazilian Norm (NB 93, 1964) sets the limits for castings between 2,5 and 3,2 μm.

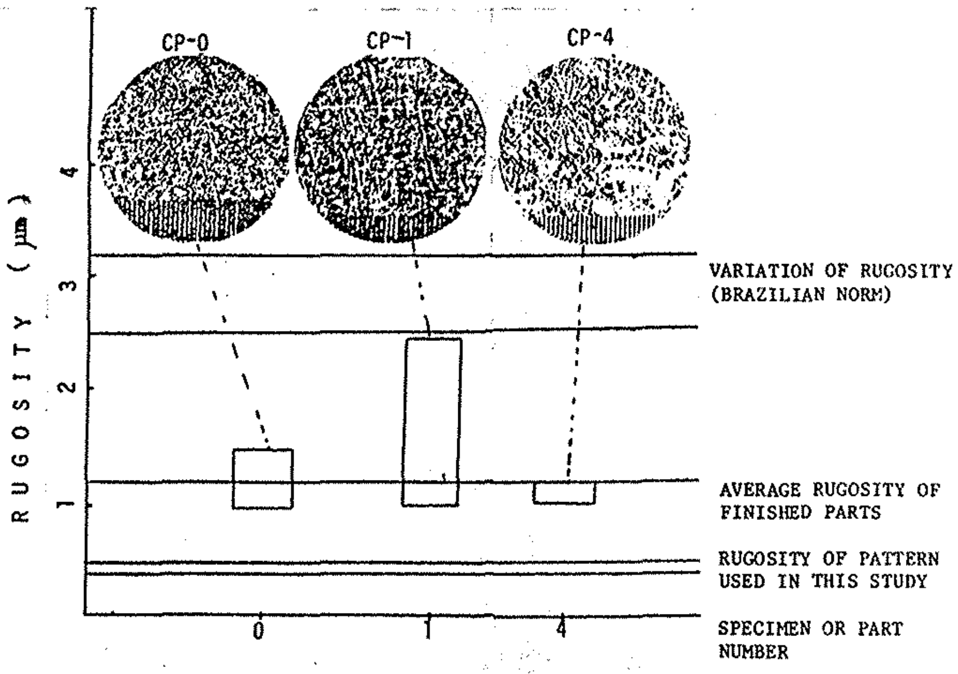

FIGURE 8. VARIATION OF RUGOSITY FOR THE DIFFERENT ALUMINUM CASTINGS.(Optical Micrographs, 11X; CP-0, No Surfactant; CP-1 with Sulfonic Acid C_{8-16}; CP-4 with Sodium Dodecylbenzene Sulfonate).

Test specimen CP-4 had a very low rugosity variation, indicating very satisfactory surface finishing. For CP-1, the rugosity fell within the required norms.

In general, the rugosity of the finished parts is higher than that of the original metal pattern (0,4 -0,5 μm). This increase in the rugosity of the copied or reproduced parts is probably the result of the various steps of the foundry process, involving microdraining of the wax and the effects of temperature, turbulence and erosion. A possible explanation of the evolution of rugosity in the finished metal parts is given in Figure 9.

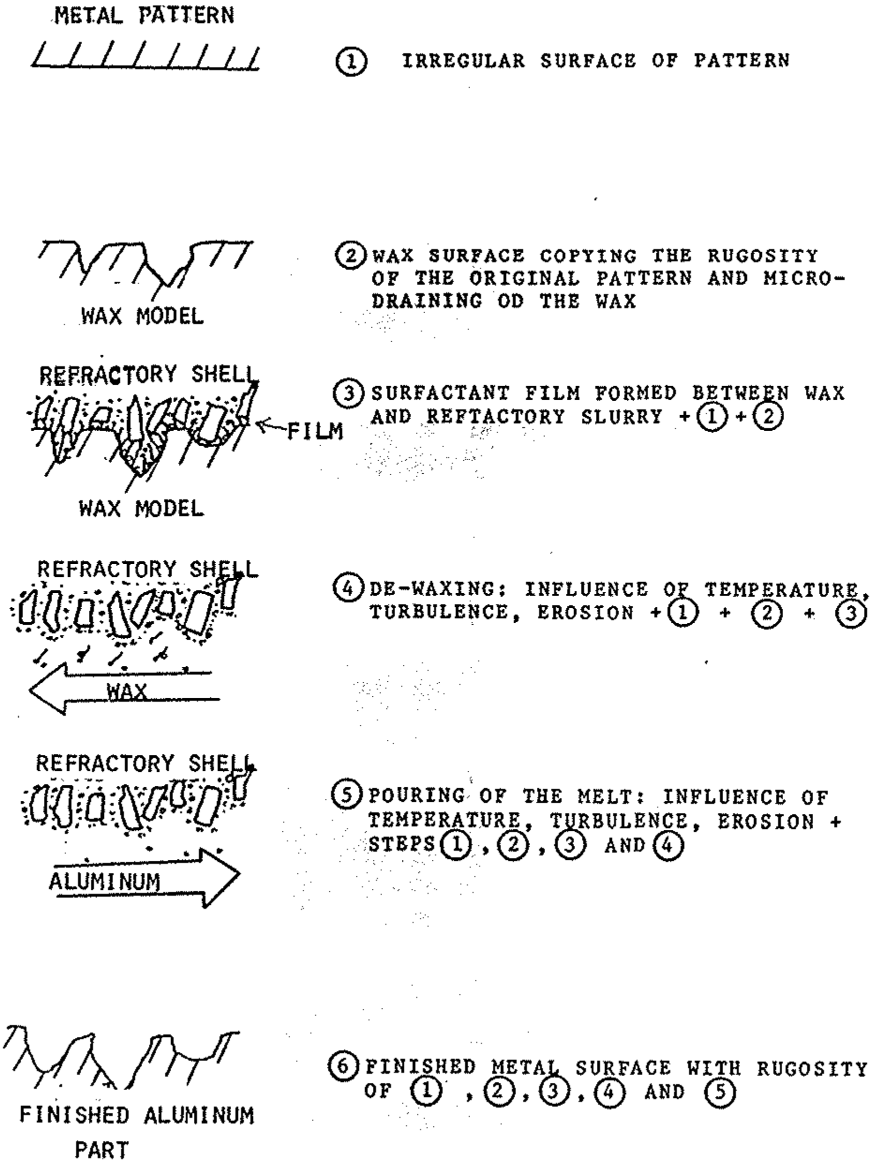

FIGURE 9. POSSIBLE EVOLUTION OF THE RUGOSITY OF THE FINISHED METAL PARTS IN PRECISION FOUNDRY.

Analysis of the experimental results leads to the conclusion that the addition of the surfactants sulfonic acid C_{8-16} and sodium dodecylbenzene sulfonate to refractory zirconite slurry greatly improves the surface quality of the aluminum castings specimens. It appears that in addition to wetting and adherence, the surfactant film or hemi-micelle layer between the soft mold and the wax model also hepls to absorb the shock during the showering of the mold with large zirconite particles, thus preserving the quality and details of the finished surface.

ACKNOWLEDGEMENTS. Financial assistance from CAPES, LAFUN and Sarmisegetusa Research Group, Santa Fe, New Mexico, USA is gratefully acknowledged.

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