AN ELECTRON MICROSCOPIC STUDY ON THE EFFECT OF CATIONIC WETTING AGENTS ON AQUEOUS STEARIC ACID SOL

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Colloidal particles of stearic acid exhibit twinkling effect under the ultramicroscope at the laboratory temperature. The effect is attributed by Ramaiah *et al.*[1] (1938) to the rod-like shape of the stearic acid particles in colloidal state. From a study on the depolarisation and extinction coefficient, Krishnan[2] (1938) has concluded that the sol contains elongated and non-spherical particles. A determination of the shape of the colloidal particles by the Langmuir technique has shown that the sol consists of disc-shaped particles (Subramania and others,[3] 1944). An electron microscopic study by Rao[4] (1950) has indicated that the stearic acid sol is a mixture of elongated and laminar particles.

We have observed that the twinkling effect of stearic acid particles persists when the sol is treated in the cold with detergents but disappears partially on boiling. The streaky appearance is, however, lost when the sol is boiled with a cationic wetting agent but persists in the case of an anionic wetting agent at small concentrations. At high concentrations of the wetting agent, however, the sol undergoes flocculation. The present work was undertaken to follow the changes of the shape of stearic acid sol particles when they are subjected to treatment with cationic wetting agents.

EXPERIMENTAL

Preparation of solutions

1. *Stearic acid sol.*—The sol used for the experiment was prepared by Mukherjee's method.[5] The concentration of the acid in the sol was 0·003%.

2. *N-butyl guanidine sulphate.*—Prepared from *n*-butyl amine and dimethyl isothio-urea sulphate by boiling with 50% aqueous alcohol. The substance when crystallised from aqueous alcohol was needle-shaped. Its melting point was 206° C. The concentration of the solution was 1%.

3. *Cetyl pyridinium bromide.*—Commercial cetyl pyridinium bromide was recrystallised from dioxane solution.

4. *Triethanol-amine hydrochloride.*—This is prepared by the action of triethanol-amine on HCl acid and crystallised from ethyl alcohol.

The samples were prepared for electron microscopic observation by allowing a drop of the sol (concentration = 0·0003%) to dry on a Formvar-coated specimen carrier kept in a calcium chloride desiccator. The sols treated with wetting agents were also mounted similarly. The procedure for mixing the sol with the wetting agent was as follows: 5 c.c. of the stearic acid sol (concentration $= 0{\cdot}0003\%$) in a clean test-tube was mixed with 0·5 c.c. of *n*-butyl guanidine sulphate solution. The mixture was shaken and allowed to stand for about two minutes. A drop of the solution was then used to prepare the specimen. Similarly, to 5 c.c. of the sol in each case was added separately 0·5 c.c. of 1% of triethanol-amine hydrochloride and 0·1 c.c. of 1% cetyl pyridinium bromide and the solutions were made up as above.

A Philips three-stage electron microscope operated at 60 KV was used to take the electron micrographs. The condenser control was adjusted to give the lowest beam intensity for visual observation at an initial magnification of 10,000 diameters. The magnification was calibrated by comparison with a standard sample of polystyrene latex (Dow latex batch 580 G, diameter 2590 A.U.). The samples were later shadowed with chromium (thickness ·40 A.U. at an angle of arc tan 1/5).

RESULTS

Fig. 1 gives the electron micrograph of stearic acid sol which indicates that the particles are elongated and laminar in shape, and are partially transparent to 60 KV electrons. Shadowing reveals that the thickness of the particles is small compared with their size. The edges of the particles are uniformly thicker than the body which suggests a raised rim. It is also found that on ageing, the sol develops much more sharp and well defined edges.

Fig. 2 is a representative electron micrograph of the stearic acid sol treated with cold solution of guanidine sulphate at room temperature. It is interesting to note that although the outline of the main colloidal particle is retained, yet a portion of the substance appears to have volatilised and condensed on the other portions of the supporting film. Visual observations also indicated the slow evaporation of the particles.

Figs. 3 and 4 give the electron micrographs of stearic acid particles treated with cold cetyl pyridinium bromide and triethanol amine hydrochloride respectively. In these cases the length of the shadow indicates that the particles are not quite laminar but thick and the edges are less sharp. In Fig. 3 it appears as though there is a tendency of the particles to coagulate. In Fig. 4 the particles seem to have no definite shape.

Figs. 5 and 6 represent the electron micrographs of stearic acid particles boiled with triethanol amine hydrochloride and guanidine sulphate respectively. They show a change in the shape of the particles. It is seen that they are no longer elongated, in fact they have developed a circular diffuse contour. Boiling also destroys the sharp edges. Coagulation is more prominent and the necks of the coagulating particles are also seen.

CONCLUSION

As stated already, the shape of the colloidal particles of the untreated stearic acid is elongated and laminar with a thickness of about 1·5 mμ. When the stearic acid is treated with the guanidine sulphate in the cold, the size and the shape of the particles remain practically unaltered (Fig. 2). But when the colloid is mixed with cetyl pyridinium bromide or with triethanol amine hydrochloride the shape of the particles is changed rapidly (Figs. 3 and 4) and there is always a tendency towards coagulation. It is probable that these two surface-active agents neutralise the negative charge on the stearic acid and bring about coagulation. In the case of guanidine sulphate on the other hand, the neutralisation of the charge is comparatively less and consequently the size and the shape of the particles remain unaffected. The cataphoretic behaviour of these particles was studied by employing Mattson's type of micro-electrophoretic cell. All the particles had a negative charge. The mobility of the stearic acid was highest while that of the treated samples diminished in the order *n*-butyl guanidine sulphate, triethanol amine hydrochloride and cetyl pyridinium bromide. The evaporation and subsequent condensation of the colloidal particles particularly conspicuous in Fig. 2 is probably due to the lowering of the melting point of the surface complex of the guanidine sulphate with stearic acid which gets evaporated by the heat of bombardment of the electrons. Similar evaporation is also reported during the electron bombardment of silver bromide during electron microscopic studies. It appears[6] that the AgBr sublimes due to the heat produced by the electron absorption and gets redeposited on the cooler parts. Literature indicates that the m.p. of AgBr is 427° C. and since the system is subjected to high vacuum, one would expect the sublimed silver bromide to be removed from the film and not to get redeposited. It is, therefore, probable that the sublimed volatile bromine salt is first decomposed ,photo-chemically into the metal and the former being a solid of high m.p. gets redeposited on the supporting film while the bromine gets removed. As stated already the stearic acid-guanidine sulphate complex with a low melting point volatilises by the heat of electron bombardment, decomposes in the vapour phase and gets recondensed as the less volatile stearic acid. The apparent redeposition of the solid can also be due, in part, to the sputtering of the solid under the electron bombardment.

When the stearic acid solution is boiled, the particles melt at about 66° and become spherical but the sphericity is again destroyed on cooling. Thus the formation of the colloid is thermally reversible. But in presence of the surface-active substance, the process becomes irreversible. The electron micrographs taken for the mixtures after boiling indicate more or less spherical particles showing thereby that the original asymmetric shape is not regained. At the same time the adsorbed detergent reacts with the stearic acid forming a surface coating on the complex. The consequent change in the interfacial tension causes the surface area of the assembly to be reduced and hence maintain the stearic acid particles in a spherical condition even after cooling. The spherical condition

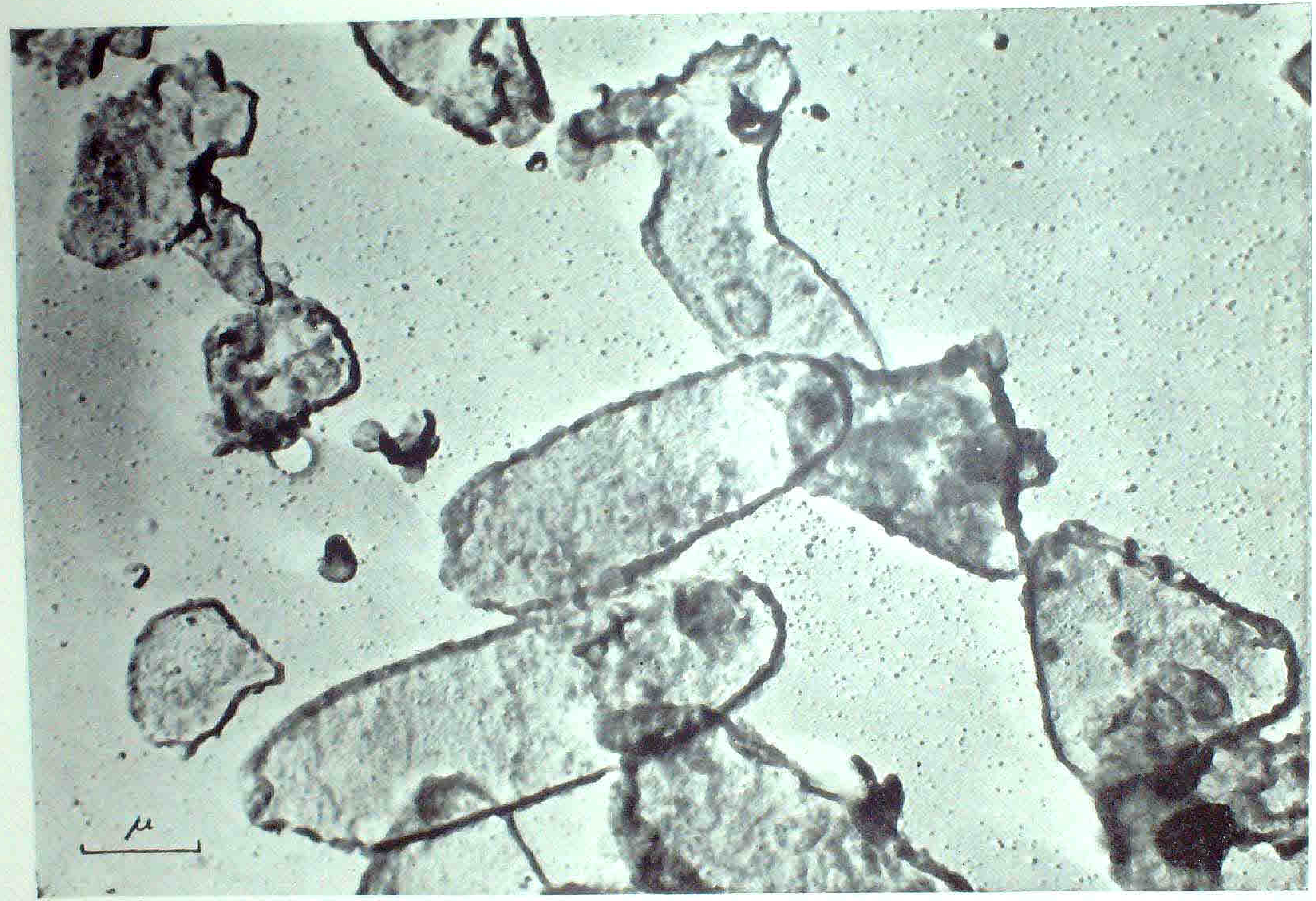

FIG. 1. Electron micrograph of stearic acid sol particles (Shadow-cast) M=15,000×

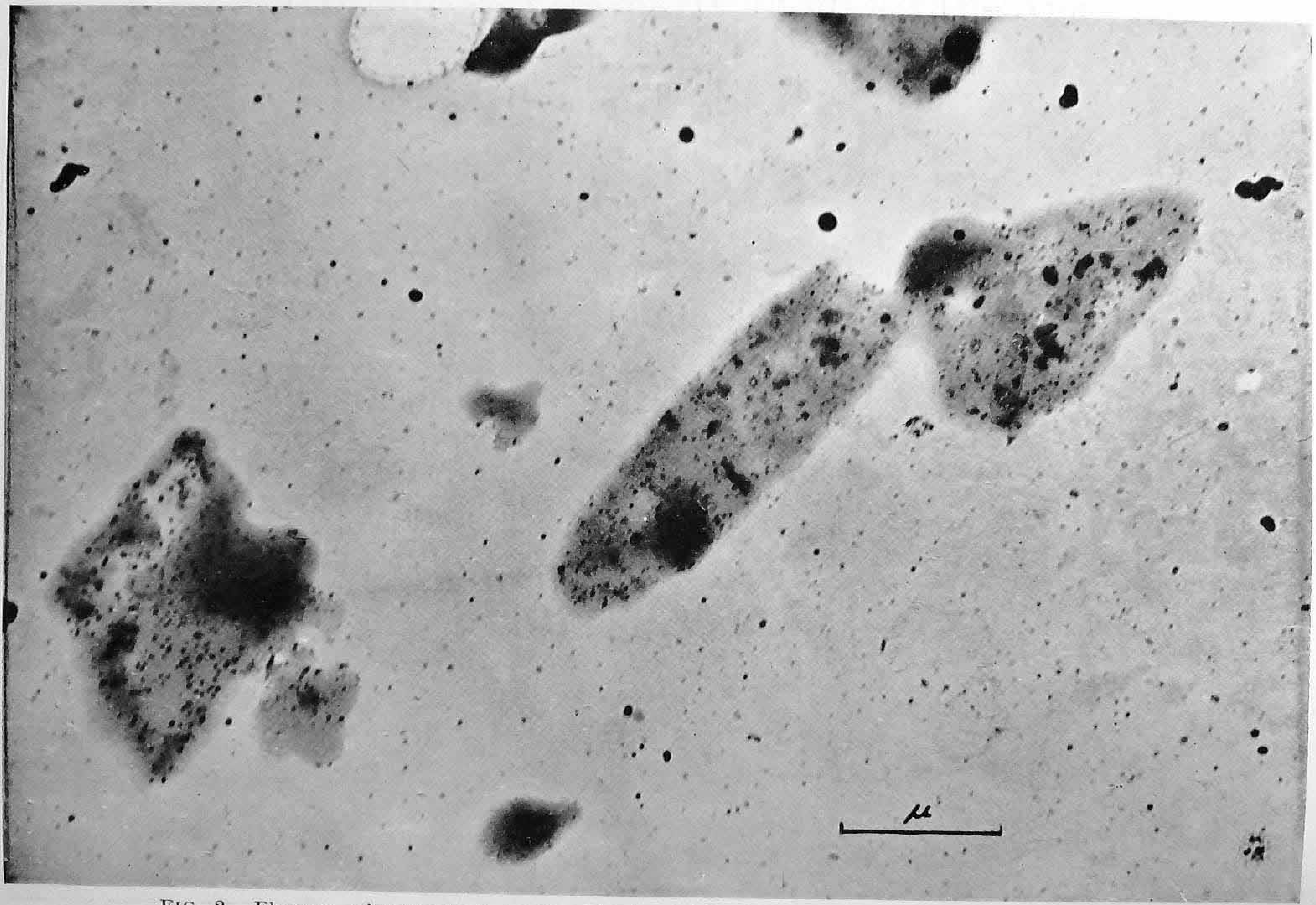

FIG. 2. Electron micrograph of stearic acid sol particles when treated with cold *n*-butyl guanidine sulphate (Not shadow-cast) M = 20,000 ×

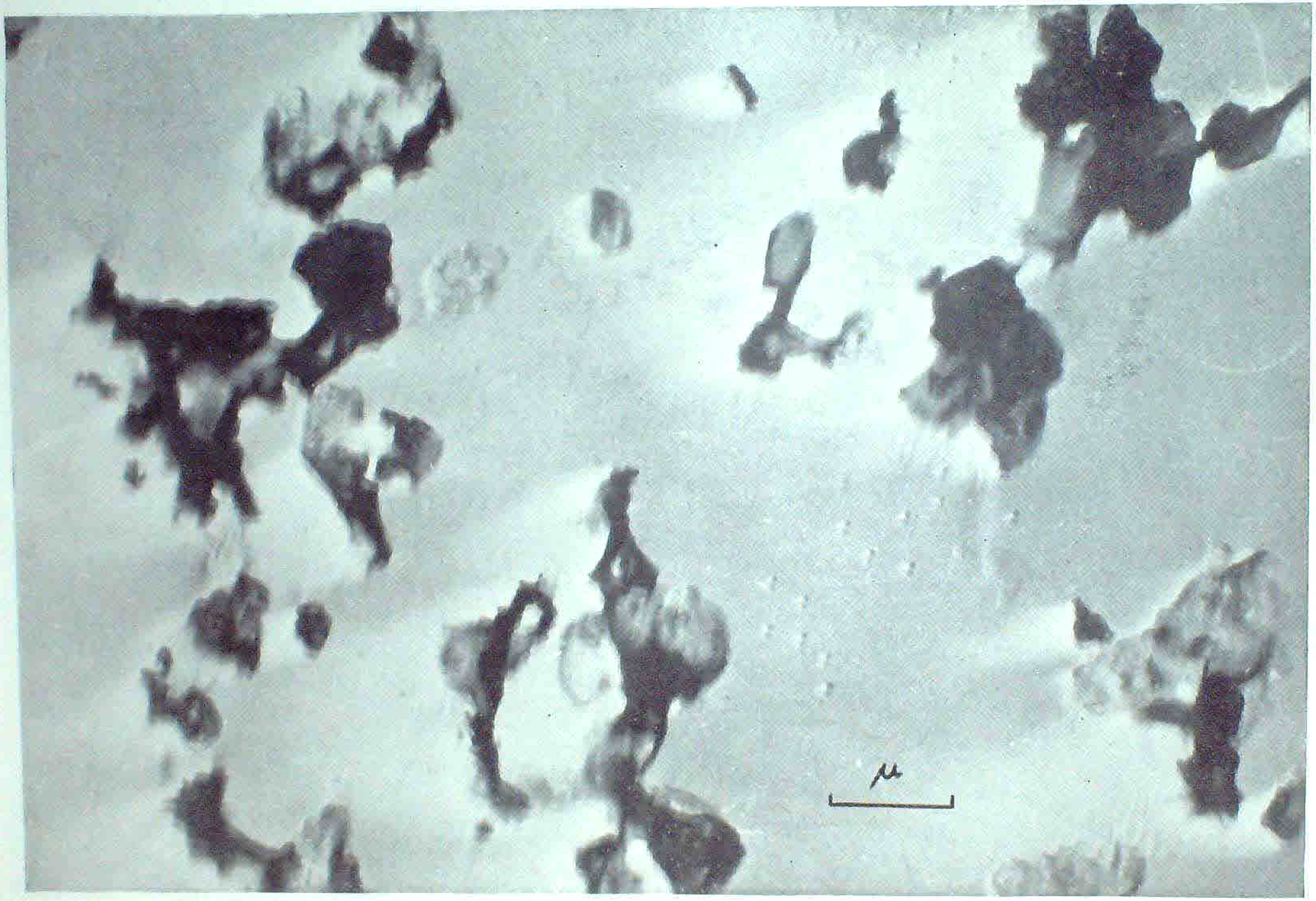

FIG. 3. Electron micrograph of stearic acid sol particles when treated with cold cetyl pyridinium bromide (Shodow cast) M=15,000×

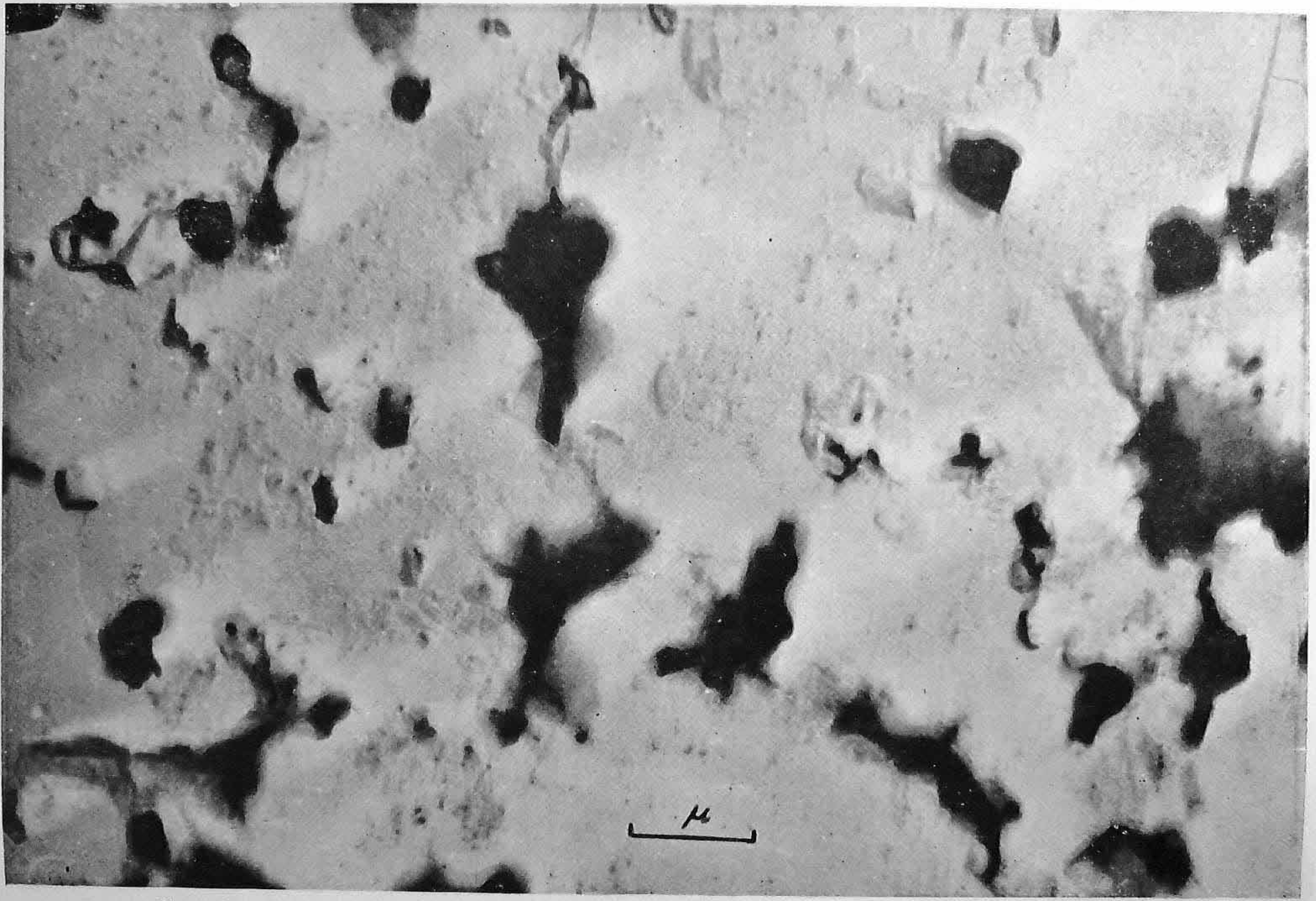

FIG. 4. Electron micrograph of stearic acid sol particles when treated with cold triethanol amine hydrochloride (Shadow-cast) M = 15,000 ×

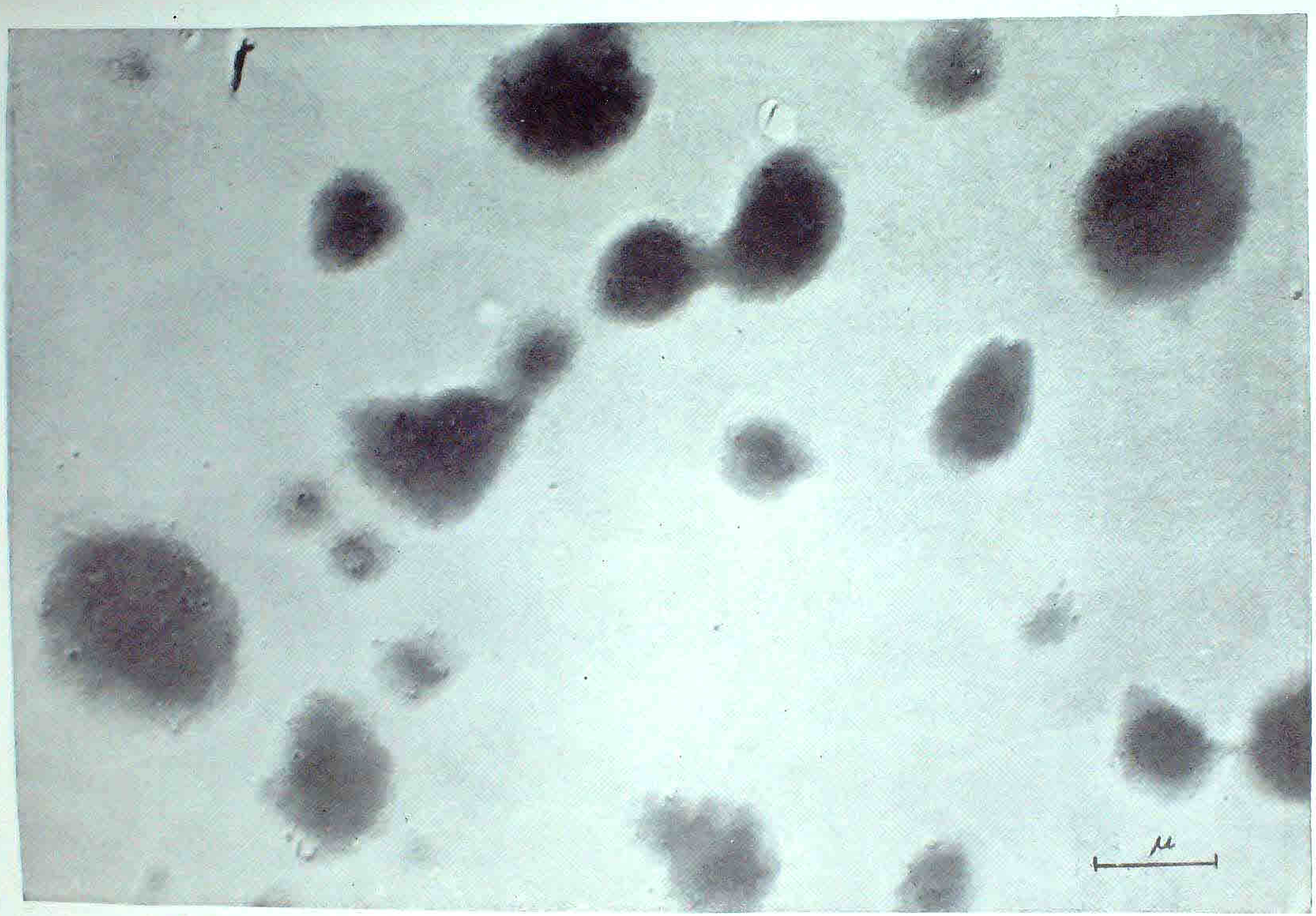

FIG. 5. Electron micrograph of stearic acid sol particles when treated with boiled *n*-butyl guanidine sulphate (Shadow-cast) M = 15,000 ×

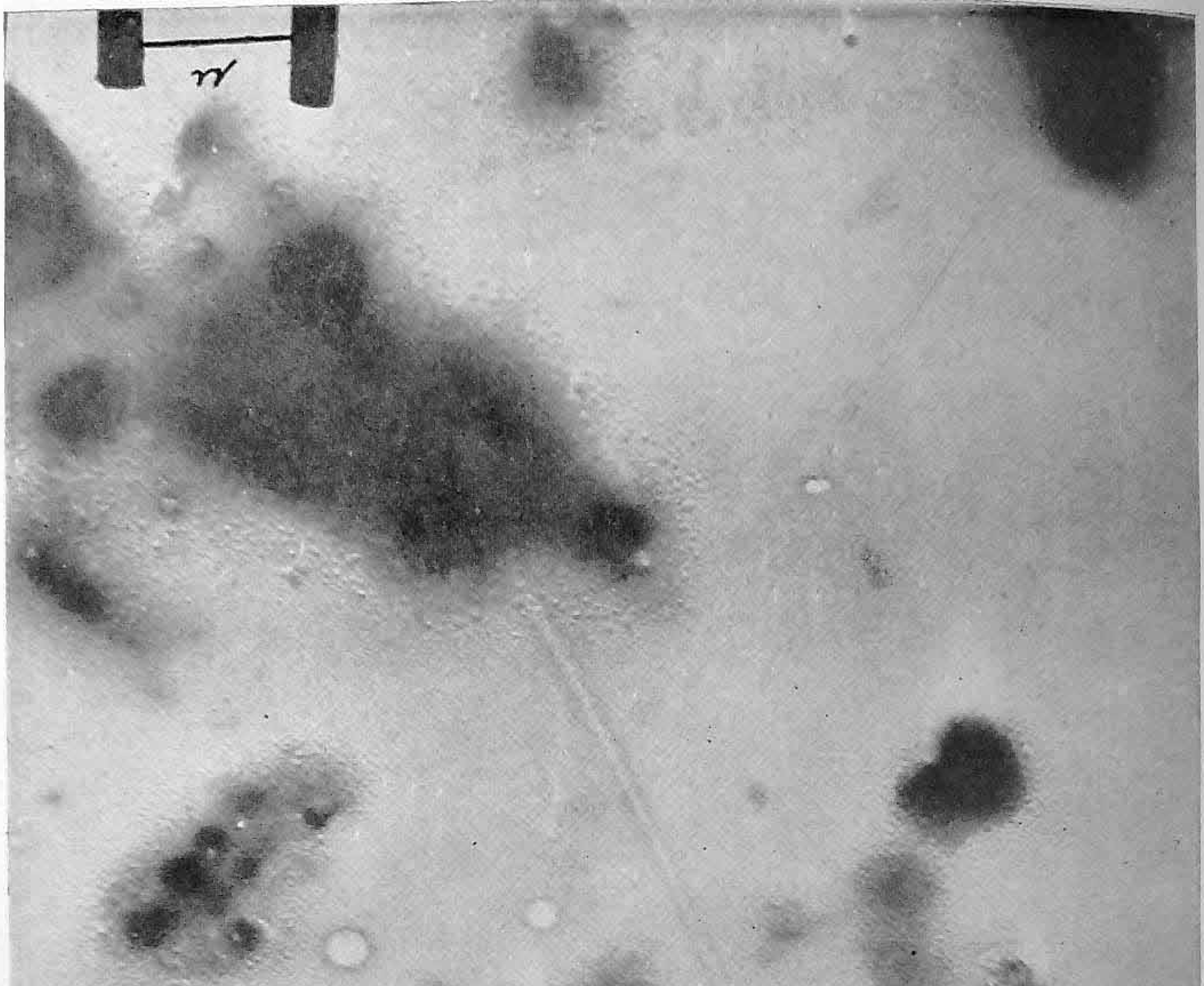

FIG. 6. Electron micrograph of stearic acid sol particles when treated with boiled triethanol amine hydrochloride (Shadow-cast) M=15,000 ×

of the particles is further confirmed by the fact that the boiled and cooled solution loses the streaky appearance on shaking the solution.

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