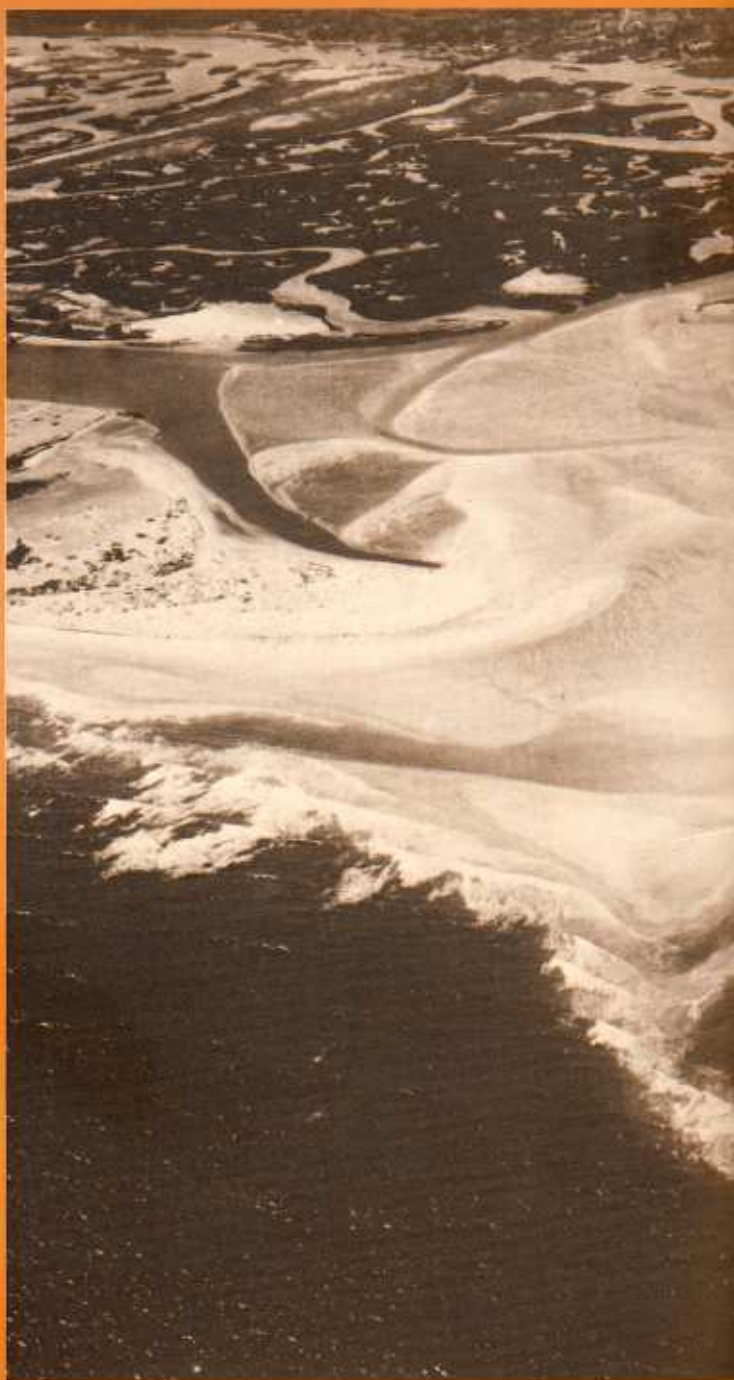# Colloids

colloids

Colloids are in some ways similar to both suspensions and solutions. In solutions solid substances are dispersed as molecules or ions in liquids, whereas in suspensions insoluble substances are temporarily stirred up with liquids. A true solution is uniform in appearance; it is impossible to distinguish the dissolved solid from the liquid solute. By contrast a suspension is visibly composed of two components which eventually separate when the solid settles to the bottom of the containing vessel. Colloids are a category of dispersions, which is not so easily defined. Milk, for example, consists partly of minute globules of fat which remain suspended indefinitely in a watery medium. In ice cream, apart from milk or cream, there are particles of ice which are so uniformly dispersed as to be unnoticed by the most sensitive tongue. Emulsion paint is essentially oily but it may be mixed or thinned with water. Even after fairly long standing, the oil does not separate from the rest of the mixture. In the air around us there are similar puzzles; fogs, mists, and clouds consist of particles of water suspended in air. Although these droplets frequently coalesce to form rain, they may remain in suspension for prolonged periods. Rivers like the Nile carry thousands of tons of insoluble clay in comparatively clear suspension and most of this clay is deposited at the mouths of the rivers when the water reaches the sea. Ancient Egyptians regarded this phenomenon as a model for the creation of the solid material of the universe from nothingness.

Milk, ice cream, emulsion paint, mists and clouds, and muddy river waters are not solutions. Yet the particles in them do not immediately settle as they do in suspensions. Sometimes the particles remain suspended for years. They are said to be in colloidal state. It is the forces which keep the particles in this state which are of particular interest to chemists.

Mud carried in colloidal
suspension in rivers settles
when it meets the salt water of
the sea at the river mouth.
Aerofilms Ltd.

Milk is one of the numerous
colloidal suspensions which we
use daily.
National Dairy Council

Cover
Colloidal particles (orange)
undergoing Brownian motion.
The large particles are
bombarded by rapidly moving
molecules (red) and execute a
zig-zag path within the system.

the properties of colloids
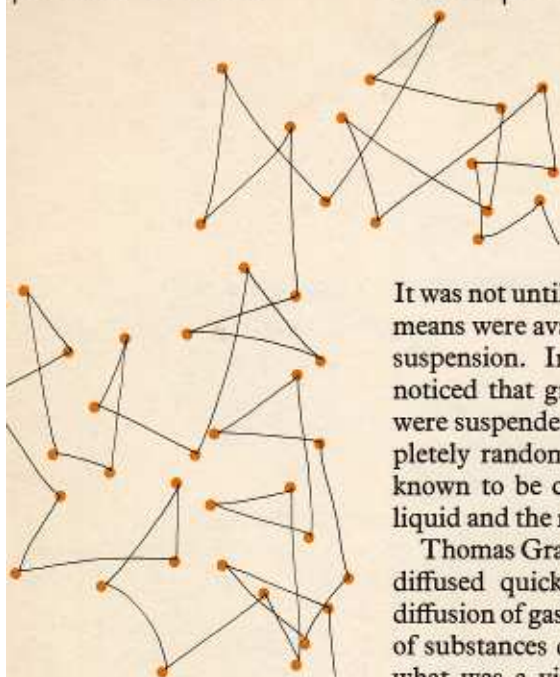
Brownian motion. If a colloidal particle were photographed at intervals of twenty seconds, a picture like this might be obtained. The particle's motion between each exposure is as erratic as that shown here.

It was not until the first half of the nineteenth century that the means were available to explain how these particles remain in suspension. In 1827 Robert Brown, a Scottish botanist, noticed that grains of pollen and other fine powders which were suspended in water jerked about continuously in a completely random manner. This 'Brownian movement' is now known to be caused by collisions between molecules of the liquid and the minute, suspended particles.

Thomas Graham (1805–1869) noticed that some substances diffused quickly and others slowly. He had been studying diffusion of gases and he extended his observations to a variety of substances dispersed in water. He laid the foundations of what was a virtually new science. Graham called the slow diffusers colloids, from a Greek word meaning 'glue-like'. The others he called crystalloids. He deduced that slow diffusion was related to the size of the particles involved. But he did not realize that the essential distinction between the two categories was not in the nature of the substances themselves but in the state in which the substances happened to occur in particular circumstances. Soap dissolved in water, for example, is in a colloidal state whereas solid soap is crystalline.

It is more precise to refer to the colloidal state rather than to colloids, although the latter term is often used loosely to describe the various colloidal suspensions. In all colloidal states there is a dispersed substance, which is called 'the disperse phase'; and there is a dispersing medium, which is often referred to as 'the continuous phase'. The disperse phase is the substance which is distributed in small particles throughout the continuous phase. Colloidal particles are intermediate in size between the particles in solutions and those in suspensions. There is no sharp limit to particle size; the particles may be aggregates of smaller particles like an iron (III)

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Sol

parchment

solvent
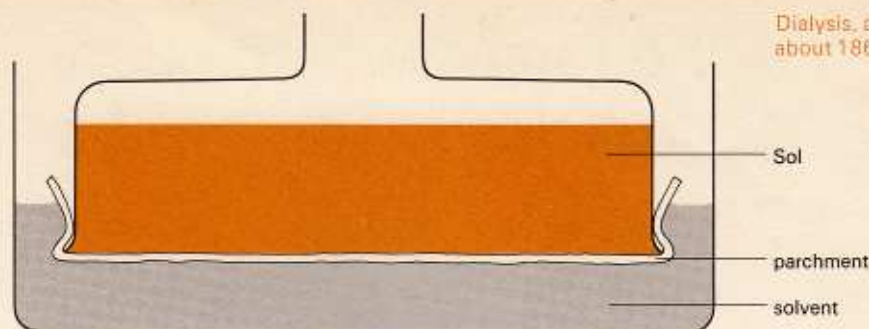
hydroxide sol, or they may be large molecules of substances like rubber or plastics or proteins. In 1908 Albert Einstein showed that the size of particles which behave like this are between 10^{-4} and 10^{-7} cm in diameter.

The combined effects of Brownian movement and the tendency of the particles to slip down through the liquid under the force of gravity produce a difference of concentration between the top of the sol and the bottom. This difference is not very great but it is the same sort of 'concentration gradient' as in the earth's atmosphere; as we ascend a mountain the concentration decreases, the air becomes rarer. Particles in this size range, suspended in a liquid, may have the same kind of movement, and the same inability to settle, as gaseous molecules.

As we examine colloids we shall see that the size of the particles does not explain all colloidal properties. Furthermore not all particles of this range of sizes enter into a colloidal state when in a liquid. We shall see that there are several possible forces which may determine whether or not particles in this range enter colloidal states.

Before attempting to define these forces we might glance at some of the typical properties of colloids, as exhibited by a common laboratory substance, iron (III) hydroxide. When we add a few drops of a concentrated solution of iron (III) chloride to a large volume of boiling water, hydrochloric acid and iron (III) hydroxide are formed to give a clear liquid which contains no visible solid material. Yet this cannot be a true solution because it precipitates when a salt solution is added to it or after standing for a long time. It is called iron (III) hydroxide *sol* to distinguish it from a true solution. It has two other special properties. First, if a beam of light is passed through it the beam shows up in the same way as the projector beam in a smoky cinema, or as the sun on a misty autumn morning.

Second, the sol is very slow to diffuse: when a layer of water is placed above it the boundary line between water and sol remains sharp for a very long time, whereas the corresponding boundary between water and a copper sulphate solution disappears quickly because of the relatively quick diffusion of the copper sulphate layer into the water.

These properties may be related, as we have suggested, to the size of the dispersed particles. A true solution will not have any effect on a beam of light because the dispersed molecules or ions in a true solution are too small; but an iron (III) hydroxide sol scatters light because, although the dispersed particles are too small to be seen by the eye, they are large enough to reflect light and too large for true solution. Large particles are also slow to diffuse, since they are heavier and more sluggish. This property of the iron (III) hydroxide sol leads to a method for the purification of the sol from the hydrochloric acid which is also produced when iron (III) chloride is added to boiling water. The entire solution is held in a parchment or cellophane bag which is then placed in distilled water. The hydrochloric acid quickly passes through the membrane into the water outside but the iron (III) hydroxide particles remain inside the bag. The membrane acts as a sieve which separates the large sol particles from the ions in solution; the process is called dialysis and is used extensively in medicine to remove salts from biological preparations.

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the forces which keep particles in suspension

Although particle size is responsible for some of the properties of colloids, there are several forces which control the dispersion of these particles in a given medium and maintain the stability of the colloid. Indicating that there are several forces which may produce colloidal states is the fact that colloidal systems vary widely in viscosity. Some are almost as fluid as the liquid in which the colloid is dispersed but others are very viscous. This suggests a variety in the factors which bring about colloidal states.

Consider two very different colloidal suspensions – iron (III) hydroxide sol and raw egg white. The iron sol is very fluid, the egg white is very viscous. Both are colloids. Viscosity is a result of attractive forces between the molecules of the disperse phase and those of the dispersion medium. This helps to explain the physical differences between the colloidal states.

Since the iron sol is very fluid, we infer that there is little interaction between its particles and water. Such a sol is called lyophobic or solvent-hating. As we shall see, its stability may be due to the adsorption of positive ions by the particles, or to the loss of hydroxyl ions. Egg white, on the other hand, is a system comprising protein molecules and water. The protein molecule is very large and it has many water soluble groups attached to its folded edges. This molecule is strongly attracted to water and the strong attraction makes the resulting sol viscous. This kind of sol is called lyophilic or solvent-loving. Egg white is a good example of natural utilization of water in colloid systems. Another such system is blood which is invaluable in the transport of nutrients to different parts of the body.

In a lyophilic sol, then, the colloidal particles are surrounded by an adsorbed layer of molecules of the dispersion medium. This layer keeps the particles apart and prevents them from joining together into larger particles and settling. Lyophilic sols do not scatter light as strongly as lyophobic sols. The reason is that lyophilic sols are optically more homogeneous. Because of the adsorbed layers, their particles behave towards light in very much the same way as the dispersion medium itself. The stability, therefore, of these lyophilic sols is due chiefly to this skin of disperse phase, which keeps the particles apart. Any change in the particles themselves is muffled by this surrounding layer and prevented from having any effect on other particles outside the layer. Whereas small amounts of an electrolyte are enough to precipitate a lyophobic sol, large amounts are required to precipitate a lyophilic sol. The ions effectively compete for the water molecules adsorbed on the sol particles and therefore destroy the 'skin'.

Occasionally particles of lyophobic sols adsorb lyophilic material. The lyophobic sol is consequently much more difficult to precipitate. The new colloidal particle is effectively lyophilic and the lyophilic colloid used to bring this about is known as 'a protective colloid'. The use of protective colloids to stabilize colloidal systems is very common: gelatine in ice cream prevents the formation of large crystals of ice; egg yolk is added to the olive oil and vinegar emulsion in mayonnaise; gum arabic prevents coagulation of colloidal carbon particles in indian ink; vegetable substances, such as tannin, have a similar effect when added to certain lubricants consisting of carbon dispersed in oil.

We can now begin to understand the forces which keep colloidal particles in suspension. The process by which molecules adhere to the surface of solids or liquids in thin films is called adsorption. Since colloidal particles have a large surface area compared with their masses, they readily adsorb liquids, gases, and ions. Silica and clay, for example, become negatively

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charged in water possibly because they adsorb hydroxyl ions
(OH^-). Similarly the iron (III) hydroxide particles we saw
earlier are positively charged; this charge may arise from the
adsorption of positive ions from solution. Just as lyophilic
particles adsorb a layer of dispersion medium which accounts
for their stability, lyophobic particles adsorb charged sub-
stances which cause the particles to repel each other and so
prevent coagulation and settling. This is demonstrated when
a lyophobic sol is placed in a U-tube with an electrode in each
limb and layers of water are added to each limb above the sol.
When the current is switched on the boundary line is seen to
move towards one of the two charged electrodes. The charge
which attracts particles to the electrodes is the charge which
keeps the particles in colloidal suspension. We can now see
that although there is wide variation in colloidal systems them-
selves, the forces which provide stability to these systems in
each case do so by keeping the particles apart. When the force
is countered by the addition of an ion of opposite charge, the
particles can come together and coagulate into larger particles
which settle as a visible sediment. This is what happens when
clay in colloidal suspension in a river meets the salt water of
the sea, or when blood is coagulated by a styptic pencil, which
contains aluminium ions each with three positive charges, or
when milk is curdled by the lactic acid produced when the
milk goes sour.

An important aspect of all colloidal systems is the pre-
dominant role of surface effects. It is activity on the surface of
colloidal particles which keeps the particles in suspension.

cathode (−) anode (+)

distilled water

iron (III)
hydroxide
sol

Electrophoresis.

Since all substances exist as solids, liquids, or gases, there are theoretically nine ways in which a disperse phase may be distributed throughout a dispersion medium. Because gases are always completely miscible with each other, they cannot form a colloidal system. In practice we recognize only eight possible types of colloidal systems:

| dispersion medium	disperse phase	type of colloid
Gas	Liquid	Fog, mist, cloud, aerosol
Gas	Solid	Smoke, dust, aerosol
Liquid	Gas	Foam : whipped cream, froth, soapsuds
Liquid	Liquid	Emulsions : salad cream, milk, emulsion paint
Liquid	Solid	Sols, gels : some paints, fruit jellies
Solid	Gas	Solid foam : pumice, meringue
Solid	Liquid	Solid emulsion : butter
Solid	Solid	Solid sols : some coloured glasses, pearls

Emulsions – The familiar action of soap in removing greasy dirt from the hands provides a clue to the structure of liquid-in-liquid colloids – emulsions. It also helps to explain why colloidal systems are stable. It is impossible to wash grease off the hands with water alone because water and grease are immiscible. The application of soap makes the removal of the grease quite easy. Soap is the sodium salt of an acid whose molecule consists of a long oil-soluble hydrocarbon chain with a water-soluble end. The water molecule is a dipole, positively charged at one end and negatively charged at the other. One end of the water molecule anchors the water-soluble end of the soap molecule. At the surface of the water, water molecules try to push the water-insoluble chain out of the way. All the chains, therefore, protrude from the surface. Because they are less attracted to each other than are the water molecules, they reduce the surface tension; in other words they effectively

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make water spread more easily, instead of tending to clump in droplets.

When the water-insoluble, oil-soluble hydrocarbon chain encounters a globule of grease the chain mixes with the grease and the water-soluble end projects from the globule. Thus the grease globule becomes enveloped with a water-soluble 'skin'. The globules of grease are now easily removed by water and they are kept apart from one another because of the 'skins'. We say that the grease has been emulsified, soap being the emulsifying agent.
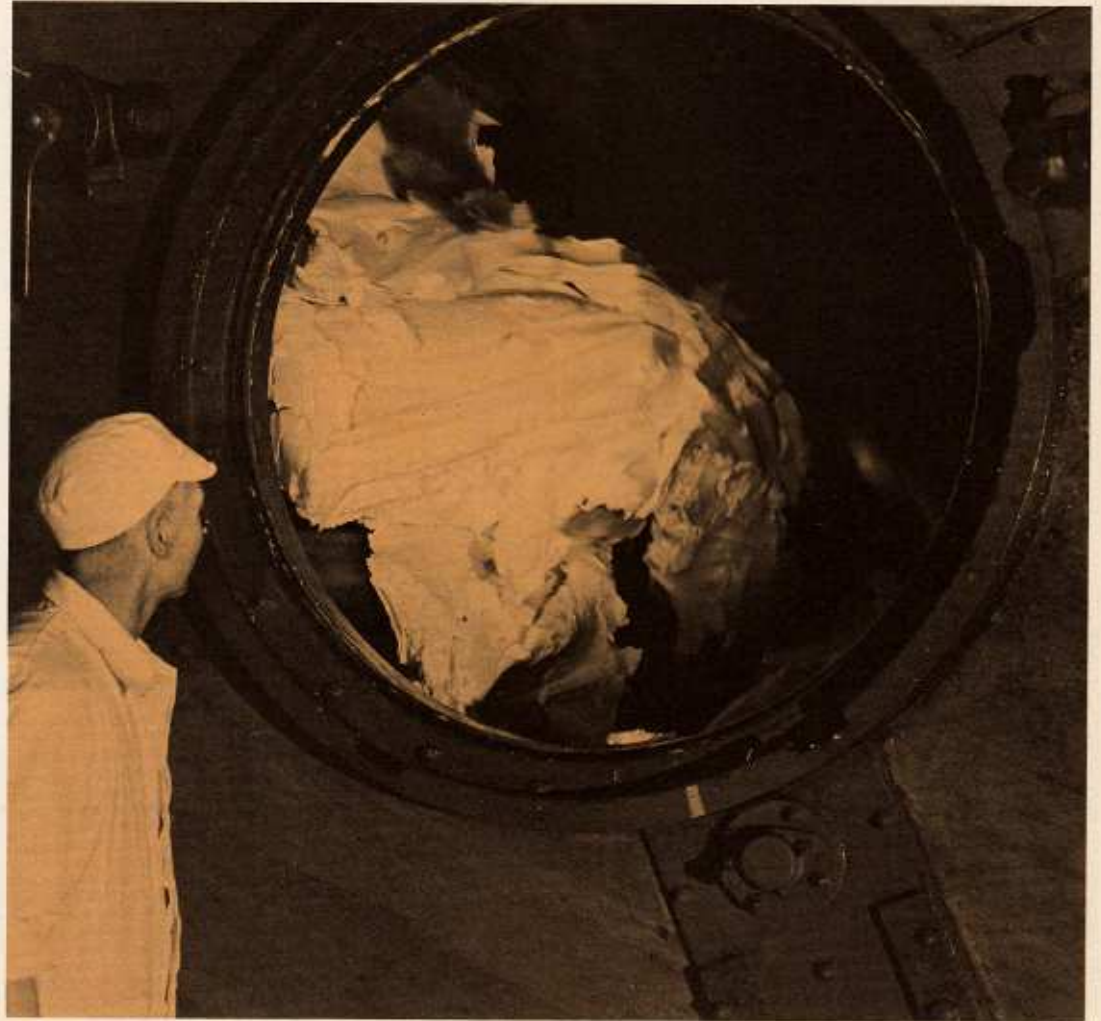
One of the most common and yet most fascinating colloidal systems is butter. The discovery of buttermaking must have come about by the accidental agitation of milk. It was an important discovery, because it is a good method of conserving supplies of edible fat, especially for nomadic tribes, and also because an emulsion of fat and water is more palatable than fat alone.

Cream, which is an oil-in-water emulsion, can be churned to butter, a water-in-oil emulsion; and butter can be reconstituted as cream. This is a reversal of disperse and continuous phases but it can only come about if boundary faces between the two phases change in energy. The controlling feature of the conversion is the emulsifying agent. This is a substance which is soluble in both the disperse and continuous phases. Its effect is to modify the comparative rate at which each of the two phases coalesces; that is, it determines which has the greater chance of forming the continuous phase. When cream churns to butter, a skin which surrounds each butter-fat globule and gives it a lyophilic character is broken and the freed fat globules coalesce. For butter to be changed back to cream an emulsifying agent must supply the skin which is necessary to keep the globules of cream apart.
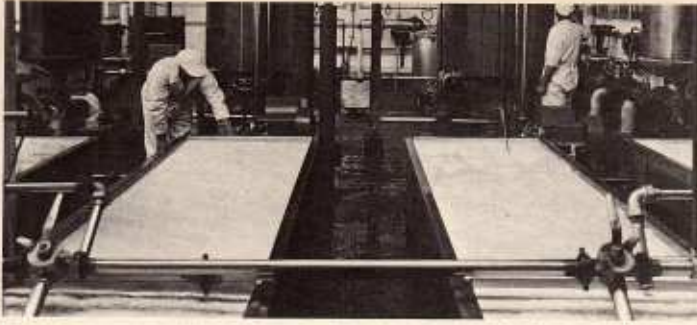
Cream about to be made into
butter.
United Dairies.

Cream that has been churned
into butter.
United Dairies.

soap molecule

represented as

soap reduces
the surface tension
of water

soap removes grease from
clothing and from the hands by
creating a water soluble layer
around the grease

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Study of this process is particularly important for making fat-water emulsions. Margarine is one example of this development. Its components are similar to butter. But butter is a water-in-oil emulsion formed naturally from cream, whereas the formation of margarine requires an emulsifier to blend together the aqueous and oil phases. Knowledge of the behaviour of these colloidal systems has led to the production of margarines which are more palatable and more nutritious than earlier kinds. These have one advantage over butter in that they spread more easily in cold conditions.

The same process can be observed when a little paraffin is shaken up with water. The two liquids subsequently separate. But if a little soap is added to the mixture, the paraffin droplets stay dispersed in the water. This technique is used in making certain medicines. Cod-liver-oil is frequently emulsified with gum acacia. The technique is also employed in the manufacture of oil sprays for fruit trees, for salad cream, in which olive oil is emulsified with egg yolk, and for those paints which, though oil-based, are miscible with water. Emulsification also plays an important role in biological processes. Bile, for

soap acts as
an emulsifying agent
on paraffin

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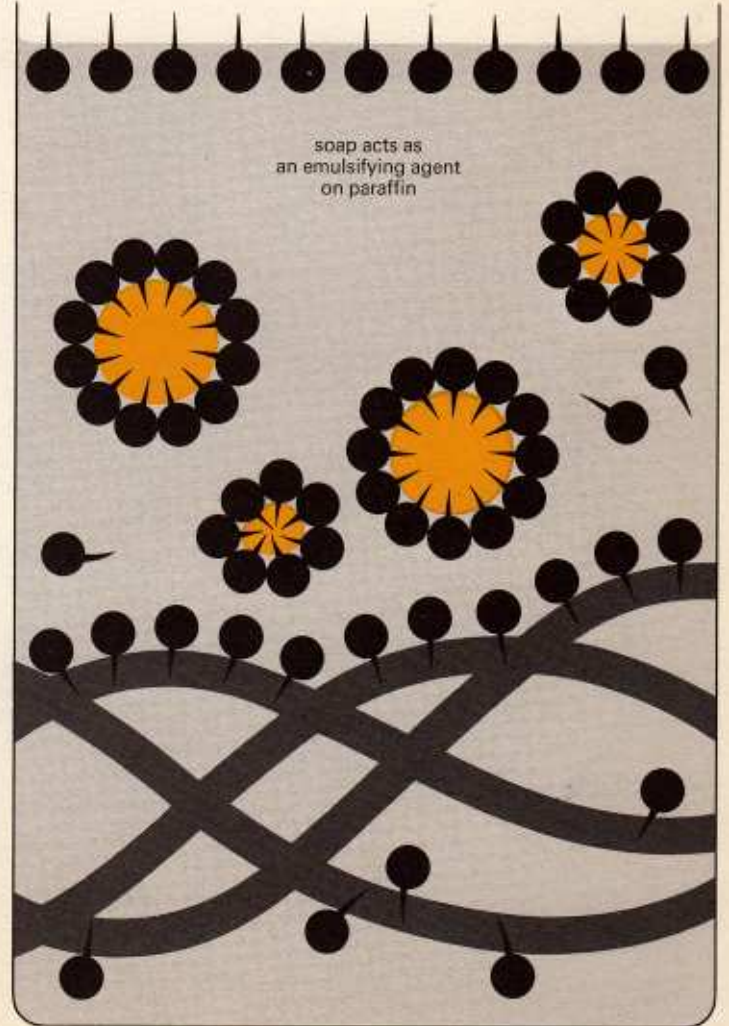
example, promotes digestion by creating an emulsion of food particles and digestive juices. Emulsification vastly increases the area of contact between them and accelerates the rate of digestion. The principle of creating emulsions to speed up chemical reactions is also used in some industrial processes. In soapmaking some preformed soap is always present and serves to emulsify fat and caustic solution.

Gels – Sometimes the bonds between particle and dispersion medium become so strong and so systematic as to form a network throughout the whole mass of the sol. These are the right conditions for the formation of a gel. Liquid molecules become trapped within the network and this makes the mass flexible, unlike a crystal which is rigid. When a solution of waterglass of suitable concentration is acidified, silica gel is formed. This is an example of an inorganic gel. Gelatin is an example of an organic gel which, in bones and tissues, provides another illustration of the importance of colloids in biology.

Modern non-drip paints are remarkable in that they are a plastic mass at rest but flow freely under stress. Similarly axle-grease, an emulsion of insoluble metal soap in lubricating oil, is fluid under pressure and fairly solid when not. Suspensions in water of bentonite, a form of fuller's earth, are used to lubricate rock drills because they set when the drill is stationary and move freely otherwise. All these are examples of *thixotropy*. The particles of the disperse phase are plate-like or rod-like in shape. They assemble in an orderly manner in a network involving water molecules, ions, and sol particles.

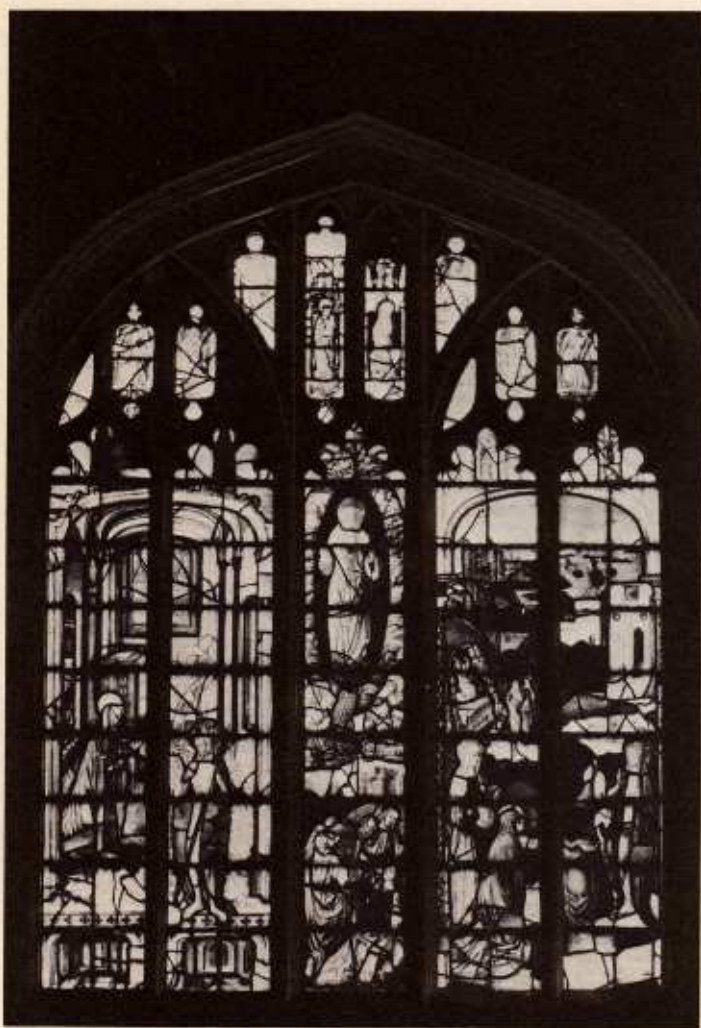Emulsion paint, which does not spill out when the tin is upset.
Lewis Berger (G.B.) Ltd.

Drilling mud used as a
lubricant in drilling for oil.
Shell.

Fruit jelly.
Rowntree and Company Ltd.

But this network remains a gel only if it is not moved. When it is shaken it moves freely and when allowed to settle it becomes semi-rigid again.

Solid sols – The best known examples of solid sols are some of the precious stones, such as ruby and emerald, and stained glasses for windows of public halls and cathedrals. The colour effects are usually due to a colloidal dispersion of metallic oxides – another example of the scattering of light by sol particles.

Foams – Surface effects are also important in foams. Foams are dispersions of gases in liquids. If the liquid in the foam should subsequently solidify the result is a solid foam such as foam-rubber cushions and expanded polystyrene.

Pure liquids do not ordinarily foam. For foams to be created there must be a surface-active agent present which reduces the surface tension and prevents the liquid of the bubble films from draining away. When the foam has formed, the effect is to increase greatly the surface of the liquid relative to its bulk. Since surface-active substances tend to move into the surface this is one way of concentrating them. Proteins are such substances; their surface activity is responsible for stabilizing foams from detergents discharged down drains; and egg-white and gelatin are proteins used to stabilize the solid foams, meringue, and marshmallow.

Stable foams are also useful in providing a 'blanket' for extinguishing fires. In the froth-flotation technique of ore purification, an ore of copper sulphide is crushed to a fine powder and placed in a flotation chamber where it is mixed with water and oil. The mixture is agitated and the air beaten

Some familiar foams:

Whipped cream.

A glass of Guinness.
Arthur Guinness & Company.

Rubber, a solid foam.
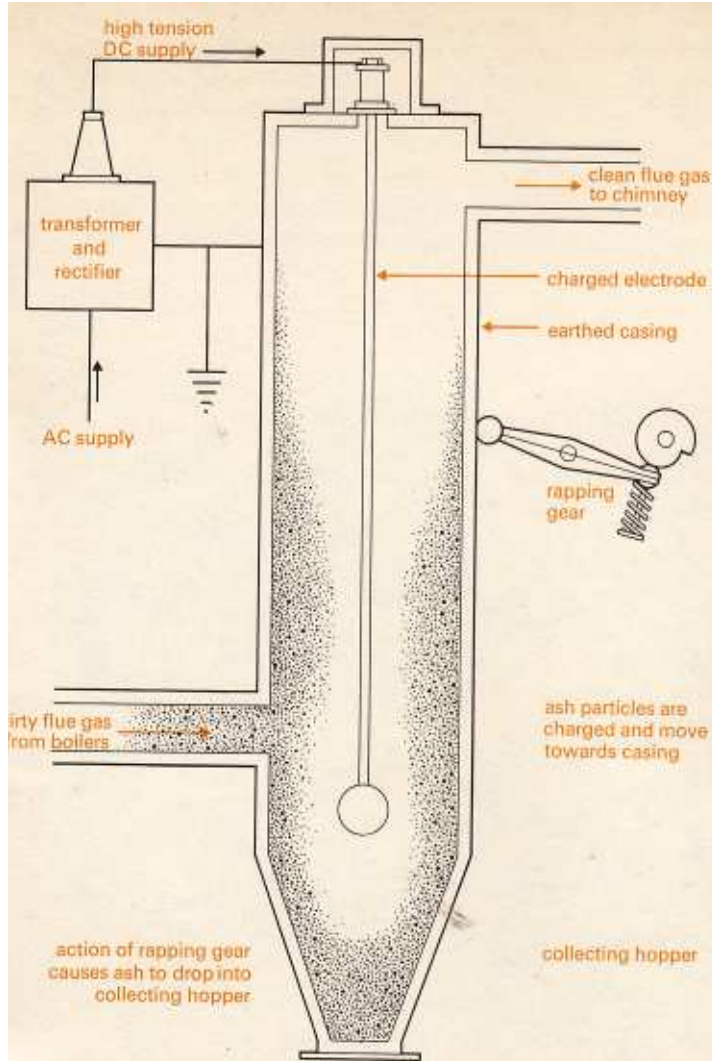*Rubber Research Institute.*

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into it forms a frothy scum on the surface. Since oil clings to the copper sulphide ore more than to rock powder, the froth is rich in copper ore. This froth is then scraped off and removed from the tank. The technique combines two types of surface activity: a stable foam is formed; and ore particles are preferentially adsorbed into the foam.

Solid-in-gas colloids – Smoke and dust from factory chimneys are very often electrically charged. Their presence in the atmosphere is not only injurious to health, it is wasteful of valuable raw materials. It has been estimated that in one day about two hundred tons of copper dust or cement dust may literally go up in smoke from a single plant. The precipitation of these particles is therefore an important problem. It has been at least partially solved by the Cottrell process. High tension wires, both positively and negatively charged, are introduced into the chimney. The dust particles are attracted to the appropriate wire; they lose their charge, coalesce, and precipitate within the chimney.

Another example of the coagulation of colloidal systems by

high tension
DC supply

transformer
and
rectifier

AC supply

clean flue gas
to chimney

charged electrode

earthed casing

rapping
gear

ash particles are
charged and move
towards casing

dirty flue gas
from boilers

action of rapping gear
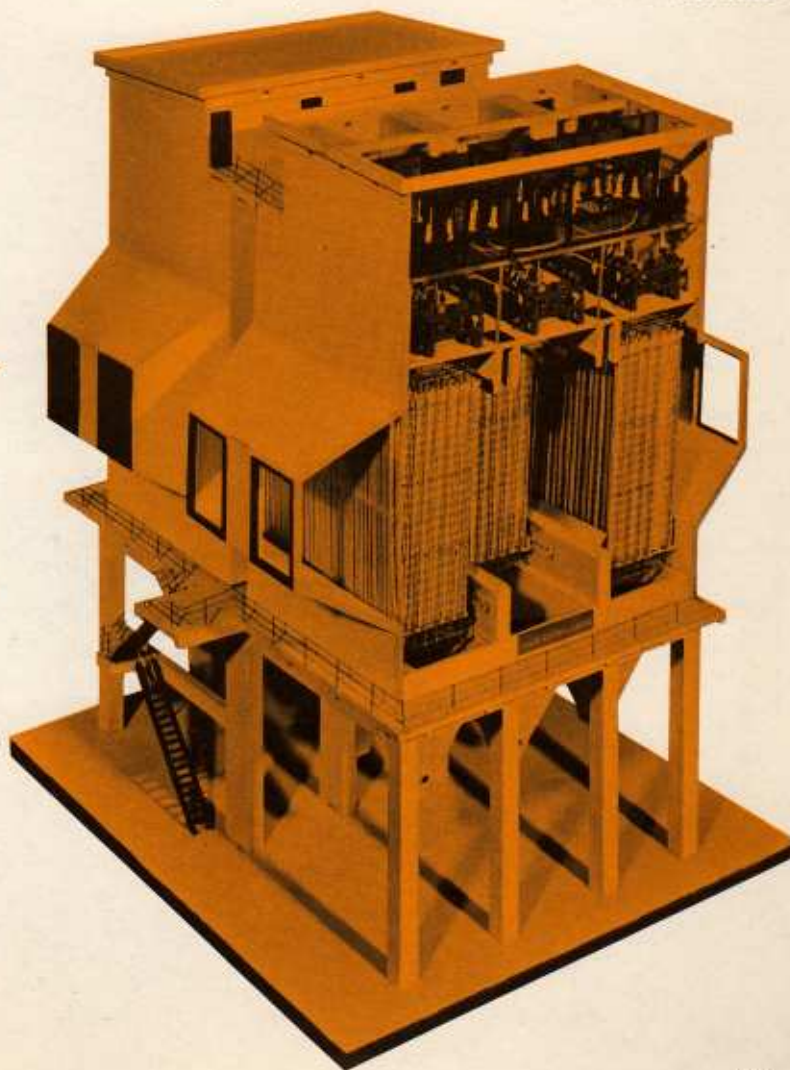causes ash to drop into
collecting hopper

collecting hopper

Froth flotation of copper ore.
Air forced up from below
agitates the mixture producing
froth. The froth eventually
overflows from the tank and
carries away the copper ore to
the next stage of the refinement
process. (Left)
Copper Development
Association.

Cottrell precipitation is used to
remove solid particles from
waste gases.
a A model of a Cottrell
precipitator. (Right)
b A schematic diagram of a
Cottrell precipitator. (Above)

electrical means is the manufacture of gloves, bathing caps, and other items from rubber latex. The latex is negatively charged colloid. It may be precipitated at the anode of an electrical cell. The thickness of the article can be controlled by time for which the current is allowed to pass through.

It is obviously not easy to give a simple answer to the question 'What are colloids?' Colloid chemistry has been defined as 'the chemistry of grains, drops, bubbles, filaments, and films'. The scope is large and the types of system to be studied vary widely – so much so that work which would once

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have been described as colloid science now permeates such university departments as soil science, food science, surface chemistry, and high polymer chemistry. Another attempt at a definition of a colloid indicates both the scope of the subject and the impossibility of rigidly defining it: 'a phase dispersed to such a degree that the surface forces become an important factor in determining its properties.'

An aerosol, producing a liquid in air suspension.
Metal Box Company Ltd.

Smoke in Middlesbrough and fog in London. Air-purification measures are making fogs less and less frequent.
Aerofilms Ltd.
Ministry of Defence.