Chemical Aspects Of Mayonnaise

An Address Before the Mayonnaise Products Manufacturers Association

BY D. M. GRAY*[1]

MAYONNAISE is seldom thought of as possessing many chemical features but a rather hasty analysis of its composition and behavior discloses the fact that it is closely linked with the chemical, and that chemistry and chemical engineering can be of great service in explaining certain features of its behavior and in overcoming certain difficulties.

In this paper, a few of these chemical aspects will be discussed briefly. To cover fully all the chemical features of mayonnaise and its constituents would be a very large undertaking and the findings would require many times the space required for this paper.

Mayonnaise dressing belongs to that class of substances known as emulsions. There are two general types of emulsions, water-in-oil and oil-in-water. It is with emulsions of the oil-in-water type that we are chiefly concerned as mayonnaise dressing belongs to this type.

An emulsion is a rather peculiar body, because while it is generally quite uniform, one of the components is in a finely divided condition while the other component is undivided or continuous and surrounds completely all of the divided portion.

For the sake of future reference we will refer to the divided portion as the divided phase and to the undivided portion as the continuous phase.

In an oil-in-water emulsion (like mayonnaise) the oil is broken up into droplets, hence it is the divided phase, while the water is unbroken, so it is the continuous phase. In a water-in-oil emulsion the water is the divided phase and the oil the continuous.

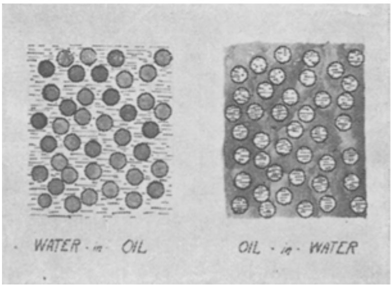

Plate 1

Craphic representation of two contrasting types of emulsions

Plate 1 is a diagrammatic representation of the two common types of emulsions. On the left, the divided drops of water are shown suspended in and surrounded by oil. For this reason, we refer to this type of emulsion as the *Water-in-oil.*

On the right is the commoner type, that of *oil-in-water* in which we are particularly interested on account of mayonnaise. In this type you will note that the drops of oil (the divided phase) are suspended in and surrounded by water (the continuous phase).

Mayonnaise dressing, milk, vanishing cream, and many pharmaceutical emulsions (cod-liver oil,

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for instance) are examples of oil-in-water emulsions. Cold cream, certain petroleum emulsions, emulsions of water with transformer oils are examples of the water-in-oil types of emulsions.

It is seldom important to determine to which type a given emulsion belongs but it can be done quite readily when necessary. One method is by testing whether or not the emulsion will conduct electricity. If it does conduct it, it is of the oil-in-water type. If not, then it is of the water-in-oil type.

In making most all emulsions, a third substance is needed, the emulsifying agent. The number of emulsifying agents is almost legion. Egg yolk and white, gum tragacanth, gum acacia, Irish Moss, casein and dextrin are the commoner, while saponin, hæmoglobin, lacmoid, pepsin, peptone, dextrine, and soap, are good emulsifying agents, though not suitable for food products. On the emulsifying agent depends for the most part, the type of emulsion that will be formed, as will be brought out in a moment.

Mechanism of Emulsification

The mechanism or process of emulsification is as follows: The emulsifying agent with the amount of water necessary to dissolve it or more water if desired is in the mixer or agitator. As the oil is added slowly with stirring it is broken up into droplets. These droplets immediately become coated with a film of the emulsifying agent—egg yolk or whatever is used. When two or more droplets touch together they remain as separate droplets, rather than uniting to form a larger drop, because they are separated by the film of egg yolk enveloping them. This film, to be sure, is exceedingly thin but nevertheless is very effective in preventing the union of the drops, unless damaged in some way, as will be discussed a little later.

In short, the whole idea in emulsification is to get the oil, or divided phase, broken up into as many fine droplets as possible, each droplet being coated with a film of the emulsifying agent.

An interesting point to consider here is the effect of a continuous and very vigorous agitation as compared to an intermittent or less violent agitation. The too vigorous agitation defeats its purpose because not only the oil but also the water is broken up into fine droplets, so that the water phase, which must be continuous, becomes a divided phase, like the oil, so that a proper emulsion can not be formed. Under these conditions the oil droplets reunite after being broken up because they are not properly coated with egg or emulsifier, since this emulsifier is dissolved in the water portion.

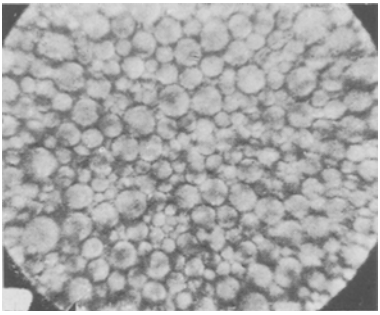

Plate 2

Mayonnaise (enlarged one thousand diameters)

By means of intermittent agitation where there is a short pause between periods of agitation, the water droplets have a chance to reunite, as there is no film holding them apart, but the oil droplets can reunite only very gradually.

Plate 2 is an actual photomicrograph in which the mayonnaise has been magnified approximately one thousand diameters. When projected on the screen it is further enlarged about twenty-five times, making the image of the particle on the screen about twenty-five thousand times the size of the particles as they actually exist in mayonnaise.

In all the following plates excepting, of course, the charts and photographs of mayonnaise samples exposed to air, the magnification is the same. You will note how the oil is in the form of small droplets, each of which is spherical in shape and is enveloped by a film of egg yolk. It is this film which prevents the reuniting of the droplets and causes the emulsion to be permanent. Each droplet is separated from its neighbors by the continuous water phase. It is this water phase which contains the acid of the vinegar or lemon juice, the salt, sugar and other ingredients not soluble in oil. The egg or other emulsifying agent is distributed in this water portion.

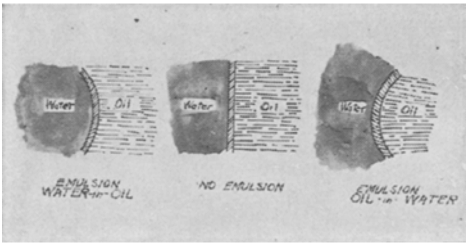

Plate 3
Diagrammatic illustration of action of emulsifying agents

In connection with the formation of mayonnaise emulsion there is a process which physical chemists call *adsorption,* not *absorption.* This covers a multitude of sins but really has some merits.

Adsorption is a concentrating or condensing of one substance on the surface of another substance but when the first substance penetrates or soaks into the interior of the second, that is absorption. A sponge may absorb water, that is, the water soaks into the interior, but a piece of glass may only adsorb the water on its surface. The reason that an aluminum griddle does not require grease in making cakes is that the air adsorbed by the oxide film on the aluminum prevents the cakes from sticking.[1] The reason that a rag moistened with alcohol can be used to clean a greasy window is that the glass surface adsorbs alcohol more readily than grease so that the grease is displaced even though it does not dissolve in the alcohol. Now, physical chemists claim that the egg is absorbed on the surface of the oil droplets in a mayonnaise emulsion. The egg does not dissolve in the oil drops but condenses or concentrates on the surface to such an extent that a protecting film is formed around the oil droplet which effectually prevents its reuniting with the other droplets.

Certain substances added to mayonnaise have a tendency to concentrate more egg on the surface of the oil or, chemically speaking, they increase the adsorption of the egg on the oil. This causes the emulsion to be thicker, and more permanent. Salt is an example of this class. Other substances decrease the adsorption (that is they decrease the concentration of the egg film on the oil). This makes the

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[1] Bancroft. "Applied Colloid Chem.," p. 82.

emulsion thinner or may break it down completely. Alum is an example of this class. More will be said of this later.

Mention was made above that the emulsifying agent had a lot to do with determining whether an emulsion of water-in-oil or one of oil-in-water would be formed. In general, emulsifying agents which are soluble in water, are adsorbed on the surface of the oil and therefore form an emulsion of oil-in-water like mayonnaise. Examples of this class are egg yolk, gum acacia, gum tragacanth, dextrin, casein, soap and saponin.

Agents which are soluble in oil, are adsorbed on the surface of the water and therefore form emulsions of water-in-oil. Examples of this class are calcium oleate, rosin, and magnesium stearate.

Plate 3 shows diagrammatically how the film of emulsifying agent bends around the droplet which it encloses. On the right—illustrating a portion of a drop of oil in an oil-in-water emulsion—the egg is adsorbed on the surface of the oil droplet, and bends around it. When this adsorption is *increased* the bending tendency is *increased.* When it is *decreased,* the bending tendency is also *decreased.* If decreased sufficiently, a condition of "no emulsion" may be reached as shown in the center. Under these conditions the egg film does not remain intact and the emulsion is broken down.

On the left, is shown a film of emulsifying agent—not egg—but one which is adsorbed on the surface of the water and is bending around the droplet of water in a water-in-oil emulsion. Such emulsifying agents are generally soluble in oil rather than water.

If substances are added to this emulsion which *increase* the adsorption of the emulsifying agent on the surface of the water, the film of emulsifying agent tends to bend more. If substances are added which *decrease* the adsorption the tendency to bend is reduced and may even reach the neutral form shown in the center.

Ingredients of Mayonnaise

For the sake of clearness, let us note the ingredients of an average mayonnaise as there are a number of points with respect to each one that should be brought out.

First, comes the oil. It may be any of the edible oils—corn, cottonseed, peanut, sesame, and others. More will be said of these oils later under the subject of Discoloration.

Next comes the emulsifying agent, egg yolk generally, or perhaps the whole egg. These have already been discussed at some length.

Then thickening agents such as starch or flour which are sometimes added. There is a word or so to be said about these under the subject of Breaking Down of Mayonnaise.

Along with this, we have the seasoning ingredients, salt, pepper, paprika, sugar, mustard, etc., which are of interest in Discoloration.

And last, we have the acid ingredients which bring most of the water content into mayonnaise. Generally, the acid is in the form of vinegar but sometimes lemon juice or citric, acetic or lactic acids are used. The effect of adding the acid ingredients is to thin down the mayonnaise to a considerable extent. The acid with its accompanying water, used in the usual amounts, does not cause the mayonnaise to partly break down, it merely flows in between the droplets of oil causing them to be at greater distances from each other. The result is that the mayonnaise is much thinner in consistency.

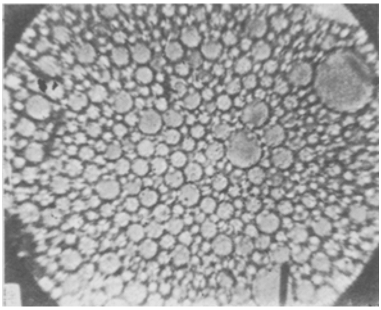

Plate 4
Heavy mayonnaise emulsion (enlarged one thousand diameters)

Plate 4 is a mayonnaise emulsion with only a small amount of water. Plate 5 shows this same emulsion after it has been thinned with vinegar. You will notice that the size of the individual particles is no greater, they are only farther apart, showing that the addition of the usual amount of vinegar does not break down the emulsion—it merely makes it more fluid by flowing in between the oil droplets. The reason that an unthinned mayonnaise is so stiff is that the oil droplets, covered with the film of egg, rub one another closely giving them a tendency to "hang together." When a little more vinegar or water is added it naturally lessens this "hanging together" tendency by flowing in between the droplets, with the result that a great reduction in consistency takes place.

One of the afflictions to which most all mayonnaise is susceptible is that of separation or breaking down, also called demulsification. This may come from one or several of a number of different causes and it is one of the purposes of this paper to outline some of the causes, their chemical explanation, and possible cures.

The first cause which we might take is that of the wrong proportion of oil, water, and egg or emulsifying agent. For a permanent emulsion of these three ingredients there seems to be a certain definite proportion for each one, which can be varied only between fairly narrow limits and still maintain a permanent emulsion. For instance, in a certain set of experiments with 78 per cent of oil, 17 per cent of water and 5 per cent egg yolk, a permanent emulsion was formed. If the amount of oil was reduced to, say, 76 per cent, the water increased to 19 per cent, the egg remaining the same, on standing the emulsion separated into two layers —a watery layer below and a creamy layer of emulsion above. If the percentage of oil was increased to 92 per cent, the egg remaining the same, the emulsion also separated on standing but this time with an oil layer above and the emulsion layer below. If the amount of oil was decreased be-

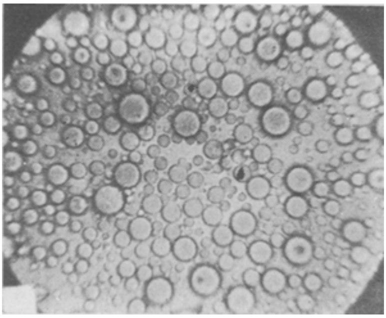

Plate 5
Emulsion shown in Plate 4, *after thinning with vinegar*

low 78 per cent and the water increased, but the egg yolk increased also, the emulsion formed was permanent. In general, the more water in an oil-and-water emulsion the more emulsifying agent is needed to make it permanent. Egg yolk was also found to have a greater emulsifying power than the whole egg.

It is impossible to give exact or even approximate ratios of oil, water and egg which will hold for all kinds and mixtures of mayonnaise because the kind of oil, the condition of the egg, or other emulsifying agent, the presence or absence and character of thickening materials, if any are used, and many other factors make each case a special one for which no general rules can be given.

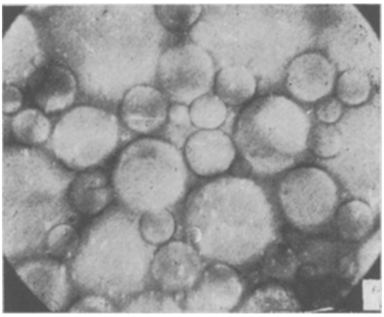

Plate 6
Mayonnaise in which oil has been added too rapidly (× 1000)

The second cause of breakdown is that due to too rapid addition of oil. Under such conditions the oil is added more rapidly than it can be broken into small droplets and coated with a film of emulsifier. The result is that the emulsion is coarse, that is, the oil droplets are large and when several of them come together they have a tendency to unite and form still larger droplets, so that we get separation of oil or at least a dressing of poor consistency.

Plate 6 shows the effect of adding oil too rapidly. The drops of oil are too large. The oil has not been properly broken into smaller droplets. The result is a dressing of thin consistency and of poor permanence.

The third cause is using the wrong kind of agitation. As mentioned above too violent an agitation is almost worse than none because it has a tendency to break up the water into droplets as well as the oil, and to prevent the water droplets from reuniting which, of course, is fatal to a good emulsion. It is scarcely worth while to do more than mention this third cause, because of the number of machines on the market which are designed especially to give the correct agitation and with which all manufacturers of mayonnaise are much more familiar than is the writer.

The fourth cause with which we are concerned is the breakdown of an emulsion due to heat. It is a well known fact that when liquids (like gases and solids) are warmed they expand and when cooled they contract. The amount of this expansion or contraction for a fixed change in temperature is called the *coefficient of expansion* and differs for different liquids. The coefficient for a certain edible oil is greater than that for water (.000721 oil and .000207 water),[1] which means that for a given change in temperature the oil will either expand or contract *more* than the water will. This causes forces to be set up in the emulsion which break the protecting egg film and force the oil droplets to unite,

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[1] Fowle 'Smithsonian Physical Tables," 1923, p. 221.

thus breaking down the emulsion. The greater this change in temperature, the greater will be the forces set up and the greater the tendency of the emulsion to separate. The finer the droplets of oil in an emulsion and the better they are coated with egg or emulsifier, the less is the tendency of the emulsion to break down when subjected to severe temperature changes.

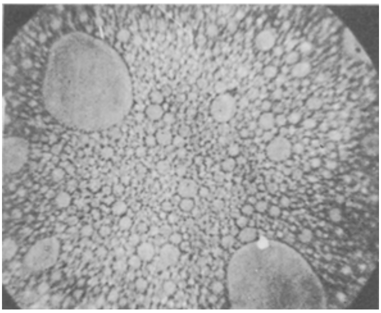

Plate 7
Mayonnaise before heating

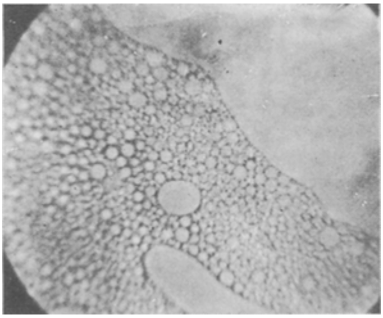

Plate 8
Same mayonnaise after slight heating

Plates 7, 8, and 9 show the effect of heat just referred to. Plate 7 is the mayonnaise at the start. The oil droplets are small, although there are several large droplets. Plate 8 shows the effect of heat, a patch of oil forming by the breaking down of the small droplets. Plate 9, taken a few minutes later on the same specimen, shows that the breakdown is increasing, as evidenced by the increased size of the oil patch.

The fifth cause of breakdown with which we have to deal is freezing. The remarks concerning the unequal expansion of oil and water which takes place during a rise in temperature apply with equal force when the temperature is reduced. When water is cooled, say, from room temperature down to 39 deg. F., it contracts. On being cooled still lower it ceases to contract and actually begins to expand so that ice is less dense than water, which is attested to by the fact that ice floats in water. Following the course of events, when mayonnaise is cooled strongly we see that the oil droplets contract to a greater degree than does the water surrounding them. This alone has a tendency to break up the emulsion. After the emulsion reaches 39 deg. F. (7 deg. above freezing) the water begins to expand. This aggravates the state of affairs greatly, so that by the time the freezing point is reached the emulsion is apt to be completely broken. When the mixture thaws the oil and water seem to have changed places, as oil surrounds fairly large patches or drops of water. In these drops, in turn, may be seen more droplets of oil. In other words, we practically have an emulsion of oil-in-water within an emulsion of water-in-oil. The mixture, of course, does not have the outward appearance of normal mayonnaise because of the separation of the oil.

Plates 10 to 14 show what hap-

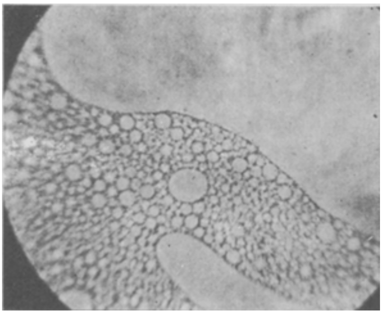

Plate 9
Mayonnaise after considerable heating

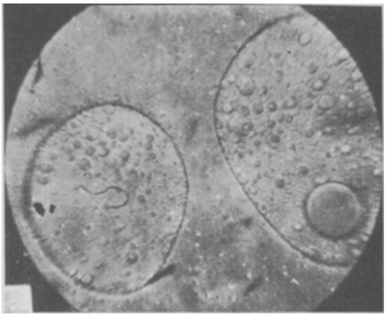

Plate 12
Frozen mayonnaise

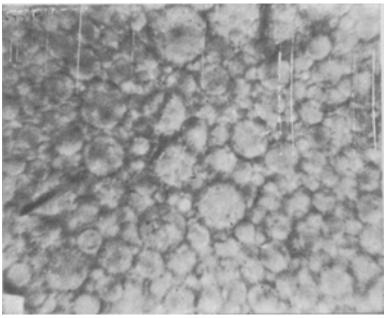

Plate 10
Mayonnaise before freezing
(× 1000)

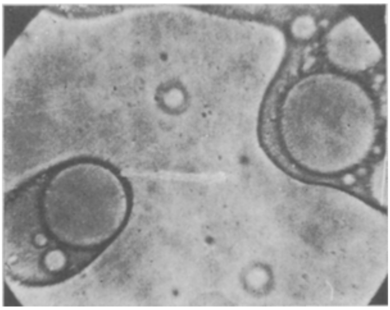

Plate 13
Frozen mayonnaise (another view)

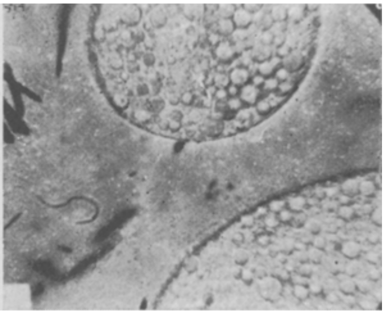

Plate 11
Same mayonnaise when frozen

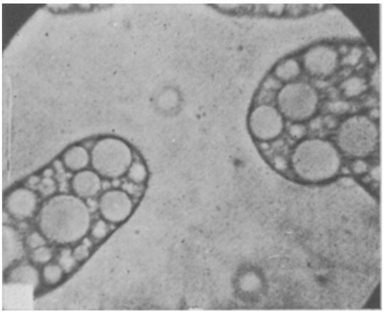

Plate 14
Frozen mayonnaise (another view)

pened when a sample of mayonnaise was frozen. Plate 10 shows the original condition before being subjected to the cold. Plate 11 shows the sample after being frozen. The plate shows that the oil surrounds drops or patches of water. Within easy reach of these patches can be seen small droplets of oil. The appearance of the whole sample reminds one of Schweitzer cheese. The cheese proper corresponds to the oil, while the gas holes in the cheese correspond to the patches of water. Plates 12, 13 and 14 are different views of the same sample. An interesting point to note here is that this peculiar appearance was noticeable in the frozen sample and as it thawed out there was scarcely any change in appearance.

Chemical Causes of Separation

The next group of causes of the breaking of the mayonnaise emulsion we may classify as strictly chemical causes. During the course of an investigation as to the reasons why a certain mixture of mayonnaise and relish broke down, it was discovered that the mayonnaise stood up well until mixed with the pickle relish. As alum causes breaking down of certain emulsions and as alum is very frequently used in pickles, the relish was examined for alum and it was found to be present. The effect of alum in mayonnaise dressing was studied very carefully under the microscope. The accompanying plates show very clearly what takes place.

Plate 15 shows the orginal mayonnaise. Plate 16 shows a solution of alum flowing into this same mayonnaise. The blurred portion is due to the moving current of alum solution, carrying along with it a number of oil droplets. You will notice that breaking down of the emulsion has already begun, as evidenced by the formation of several large oil drops. The flow of alum solution into the sample was secured by placing the end of a small strip of absorbent paper under one edge of the cover glass, which is a small disc of very thin glass covering the mayonnaise under examination. The alum solution was placed on the other end of the paper and was thereby drawn under the cover glass and distrib-

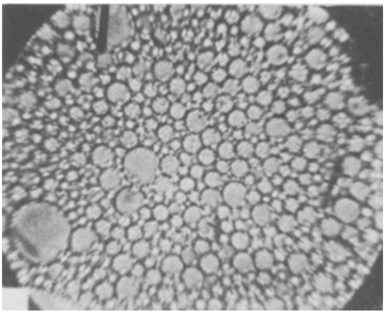

Plate 15
Mayonnaise before addition of alum
(× 1000)

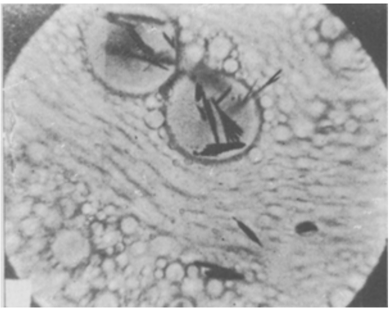

Plate 16
Alum flowing into mayonnaise emulsion

uted throughout the mayonnaise sample. Plate 18 shows, in the same manner, the effects the alum has brought about in breaking down the emulsion, that is, in causing the small droplets of oil to unite and form larger ones.

The peculiar particles seen in the oil drops in plates 16 and 18 are crystals of an oil soluble dye. This dye was dissolved in the oil to give it a color contrasting with the water portion to give better results in photographing. Some of this dye crystallized in the oil as shown, but this does not affect the behavior of the emulsion.

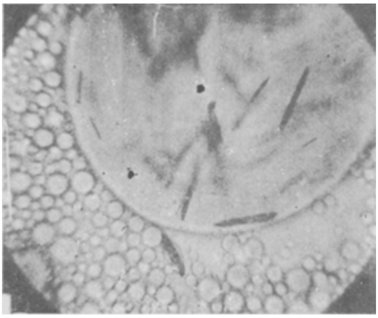

Plate 18
Mayonnaise emulsion separated by addition of alum

Plate 21 shows the emulsion about to reach the neutral point. The drops are seen to be losing their spherical shape and are forming in irregular masses. Plate 22 shows that the neutral stage has been reached. In other words, the emulsion has ceased to be an emulsion—it is a mixture in which the oil and water are intermingled in the form of large and irregular patches.

The effect of salt is just opposite to that of alum. When a little salt is added to mayonnaise it causes a very noticeable thickening. This thickening is found to be due to the droplets of oil having become more completely emulsified.

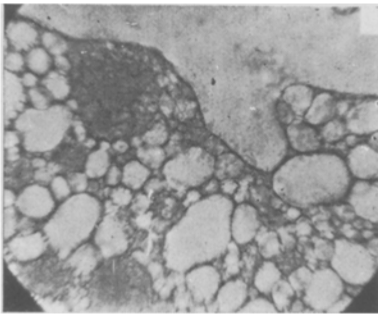

Plate 21
Same emulsion at point of complete separation

Plate 23 shows a mayonnaise which has been purposely made up in the form of a coarse emulsion by adding the oil rapidly during mixing. After all ingredients were added it was beaten five minutes longer so that if the emulsion was going to become finer it would have an opportunity to do this before the salt was added. About 1 per cent of salt was then added, the mixture beaten a few seconds to thoroughly incorporate the salt, with the result shown in plate 24. The effect of the salt

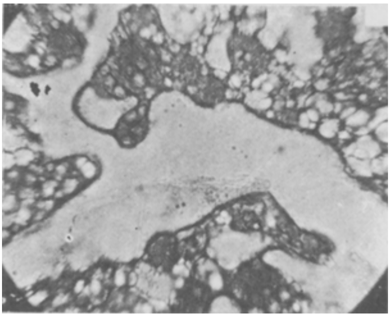

Plate 22
Same emulsion entirely separated

was to cause the formation of a much finer and more permanent emulsion, as evidenced by the reduction in the size of the oil droplets. This reduction in size explains why the emulsion became so much stiffer in consistency—because the smaller droplets can get closer together and come nearer at more points. In general, the whole structure is more closely knit and therefore stiffer in consistency.

The question naturally arises, "Why does alum cause this breaking down while salt causes thickening?" For the explanation we must again refer to adsorption—that phenomenon which takes place where the surface of the oil droplet and the surface of egg solution in water, meet. Common salt is a compound containing the element sodium. This sodium carries *one* charge of positive electricity. Alum is a compound containing the element aluminum. This aluminum carries *three* charges of positive electricity. Now, a little bit of positive electricity does not hurt an emulsion; in fact, it helps make it more stable, as we have seen above, with common salt, but when very much positive electricity gets into the emulsion it has a great tendency to break down the emulsion and cause the separation of the oil.

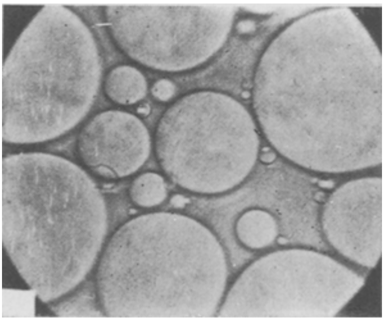

Plate 23
Mayonnaise with heavy oil-drops due to rapid mixing (× 1000)

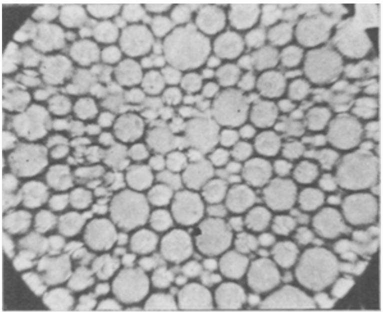

Plate 24
Same mayonnaise after incorporation of 1% *of salt* (× 1000)

The reason for this is that the charges of positive electricity are adsorbed at the surface between the oil and egg and have a tendency to break down the protecting film around each oil droplet. The more charges of positive electricity adsorbed at the surface, the more the emulsion will break down.

Plate 24-A illustrates the relative amounts of different chlorides required to break down an emulsion of oil-in-water to the same extent.[1] As we saw before, a small amount of salt (sodium chloride) was beneficial to an emulsion of oil-in-water. However, if the amount of salt added is very great it will have a tendency to break down the emulsion. Needless to say, long before this much salt is added the extreme saltiness of the mayonnaise would render it unfit for consumption. We note from the chart that it takes approximately 300,000 parts of salt to equal 6,000

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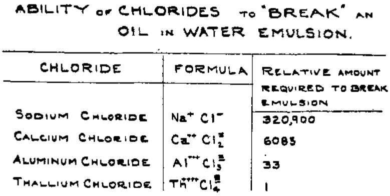
[1] Derived from table due to Powis-Clayton, "The Theory of Emulsions and Emulsification," p. 26 (1923).

parts of calcium chloride or 33 parts of aluminum chloride (similar chemically in many respects to alum) or 1 part of thallium chloride. In other words, thallium chloride, with its four charges of positive electricity attached to the thallium, is the most potent in breaking down the emulsion, while salt (sodium chloride), with its single charge of positive electricity attached to the sodium, is least potent; in fact, just one three hundred and twenty thousandths as effective.



ABILITY OF CHLORIDES TO "BREAK" AN OIL IN WATER EMULSION.

CHLORIDE	FORMULA	RELATIVE AMOUNT REQUIRED TO BREAK EMULSION
SODIUM CHLORIDE	$Na^{+}Cl^{-}$	320,900
CALCIUM CHLORIDE	$Ca^{++}Cl_2^{--}$	6085
ALUMINUM CHLORIDE	$Al^{+++}Cl_3^{---}$	33
THALLIUM CHLORIDE	$Th^{++++}Cl_4^{----}$	1

Plate 24a

Showing effect of relative positive valency on action of metallic chlorides on oil in water emulsions

Of more practical interest is the relationship between the sodium and the aluminum compounds. From these figures we may properly expect alum to be approximately ten thousand times as powerful in breaking down an emulsion as is common salt. This sheds light on the question of the small amount of alum in pickle relish exerting such a strong breaking down effect on mayonnaise when mixed with it. In general, with groups of compounds wherein the metals show an increasing number of positive charges we may expect a greatly increased "breaking" effect on oil-in-water emulsions.

Another cause contributing to the breakdown of mayonnaise is that which may occur when thickening agents are used, such as starch or flour. This is due to the action of the acid in the mayonnaise on the starch or flour and is known as "hydrolysis." One of the best known commercial examples of this type of hydrolysis is the manufacture of corn syrup or "glucose," where corn starch is treated with dilute acid which converts it into the sugar, "glucose."

The immediate effect of this hydrolysis of the starch or flour in mayonnaise is to make the dressing much thinner and watery, since a sugar solution is thinner than a starch or flour solution, both having the same water content. If the starch or flour is depended upon to keep the oil emulsified the emulsion is apt to break down, with separation of the oil. In any event, the effect is apt to be bad, because when a manufacturer makes up a dressing of the proper consistency he wants it to be that same consistency when used by the ultimate consumer.

Another cause of breakdown along somewhat the same lines is that due to the spoilage or decomposition of the emulsifying agent. Certain emulsifying agents have a tendency to decompose rapidly, consequently losing their emulsifying power, so that the emulsion breaks down. The remedy here is to use a different emulsifying agent or add an artificial preservative to keep the emulsifying agent from decomposing.

Another cause of separation of oil is due to the evaporation of the moisture from the mayonnaise. As the moisture evaporates from the surface, the protecting egg or emulsifier film dries out also, becomes brittle and breaks, allowing the oil droplets to flow together so that a layer of oil forms on the surface of the mayonnaise. Separation of oil from this cause is easily overcome, of course, by using such a closure on the mayonnaise that evaporation is prevented.

A cause of breaking down of emulsions which is seldom considered is vibration. An emulsion is a peculiarly constructed body and for that reason is sensitive to unusual influences. Ayres[1] mentions an instance where an emulsion (not mayonnaise, however) was subjected to heating, freezing and centrifuging but could not be broken down. A short ride in an express train caused it to separate completely. This is merely mentioned as a matter of interest and might be useful when all other possible reasons in a case of separation have been looked into.

The question is often asked, "Why is it so difficult if not altogether impossible to re-emulsify mayonnaise which has separated?" If the emulsion has been broken by heat, the chances are that the egg has been changed so that it does not have its original emulsifying power. If by freezing then the egg is not changed after it thaws out but the oil is distributed in large patches. If the oil, egg, and other ingredients could be completely separated, and then remixed in the usual manner, adding the oil slowly, a normal mayonnaise could doubtless be made. The same applies to breakdowns due to too rapid addition of oil, improper agitation, and vibration. If the breakdown is due to alum or similar compounds, they would have to be removed before a permanent emulsion could be formed.

If due to hydrolysis or decomposition of the emulsifying agent, it cannot be re-emulsified unless more emulsifying agent is added and a new start made.

Discoloration

The next subject with which we have to deal is Discoloration or Darkening. Very little is known about the actual causes of discoloration. Certain brands of mayonnaise darken rapidly when exposed to air, while others show only a slight discoloration. As this darkening or discoloration occurs only on the surface which is actually exposed to the air, it must be due to some action of the air on the product. The most active element in the air is oxygen, so that one would naturally attribute the darkening action of the air to the oxygen which it contains.

It is a well-known fact that certain oils absorb oxygen from the air. In other words they oxidize. In this process they change from their oily nature into a tough leathery film. They are said to "dry" and oils which have this property to a pronounced degree are called drying oils. Linseed is the most familar example of this class. Oils which have this property in a lesser degree are called semi-drying oils, and those which do not show any appreciable drying are placed in the non-drying class. There is no sharp distinction between the classes.

Plate 25 is a chart showing the amount of oxygen which various oils absorb under the same set of conditions. Linseed, of course, heads the list with an oxygen absorption of 16 per cent. Next comes corn oil with about 10.6 per cent, cottonseed with about 9 per cent, sesame 8 per cent, peanut 6.5 per cent, olive 5.25 per cent and paraffin oil practically zero.

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[2] J. S. C. I. (1916), 35, 678.

Bear these relative amounts in mind, as we will refer to them in just a moment. Neither linseed nor paraffin oil are, of course, edible, but are given here by way of comparison as they represent the two extremes.

Samples of mayonnaise dressing were made up alike in all respects except that a different oil was used in each. Corn, cottonseed, peanut, olive and paraffin oil were used. These samples were exposed to the air in shallow glass dishes and the discoloration noted after 24 and 48 hours.

Plate 26 shows one of these shallow glass dishes which has been filled with mayonnaise and exposed to the air. In the plate the discolored portion shows black, but, of course, this actually was a dark yellowish brown. The light spot in the center is the portion of mayonnaise which was covered at the outset of the test with a very thin cover glass. This protects the surface of the mayonnaise immediately under it from the action of the air and as it prevents this portion from discoloring, serves by way of comparison to tell at a glance just how much discoloration has taken place on the exposed surface.

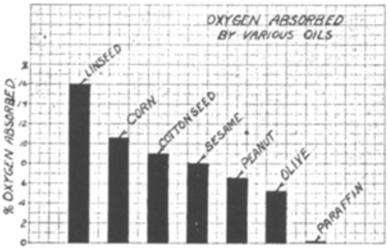

Plate 25

Relative oxygen absorption of various oils

The examination shows that the extent of darkening is in proportion to the oxygen absorption of the oil. In other words, the more oxygen that the oil has a tendency to absorb the greater will be the discoloration of the mayonnaise made from that oil.

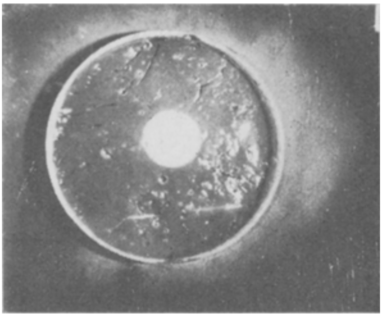

Plate 26

Effect of air-exposure in darkening mayonnaise

Plate 27 shows the relative darkening of the samples made up with the different oils. The oils used constitute the only differences between the respective samples, so that any differences in discoloration must be due to different behavior of the respective oils. The sample made with corn oil shows most darkening, cottonseed next, peanut next, and paraffin oil least. By referring again to Plate 25, we see that this is in the order of decreasing oxygen absorptions. In other words, this test showed in general that the higher the oxygen absorption value of an oil, the greater the darkening or discoloration of the mayonnaise made from it when exposed to air. Certain other factors influence the darkening as will be noted later but the relation of oxygen absorption to darkening is of fundamental importance and should not be lost sight of.

Paraffin oil is practically non-oxygen absorbing so that we shall expect it to show the least discoloration and the experimental facts prove this to be correct. Paraffin oil is used here because it *is* non-oxygen absorbing, and serves as a check on the other oils. Inasmuch as even *some* discoloration occurs on mayonnaise made with paraffin oil, although the discoloration is least of all the oils, there must be a factor besides the oxygen absorption of the oils. Therefore, it must be true that some of the discoloration is brought about by exposure of the egg to the air.

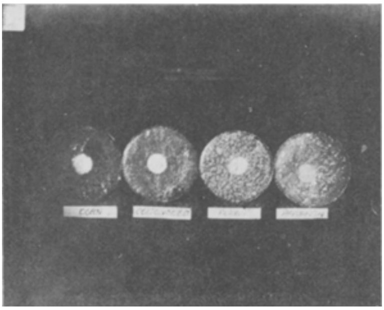

Plate 27
Comparative darkening under air-exposure of mayonnaise mixtures made from various oils

Some experiments were then undertaken to determine the effect, if any, of the other ingredients on discoloration. By other ingredients we refer to the ingredients beside oil, egg, and water; namely, salt, vinegar, mustard, pepper, paprika, lemon juice, sugar or any other added material.

Samples of mayonnaise were made with cottonseed oil, which shows moderate but not excessive darkening. To different samples were added ordinary vinegar, sterilized vinegar, acetic acid of the same strength as the vinegar used, lemon juice, citric acid of the same strength as the lemon juice used, mustard, pepper, and paprika. Samples were also prepared with and without salt, and with water in the place of vinegar.

The summary of these tests was:

First.—An ordinary amount of salt (1%) does not appear to increase or decrease discoloration.

Second.—Sterilized vinegar gave no improvement over ordinary vinegar. This test was carried out as it was thought possible some of the darkening might be due to bacteria or other organisms in the vinegar.

Third.—Samples made with acetic acid of the same acid strength as vinegar were found to discolor less than those made with vinegar.

Fourth.—Citric acid showed a very slight improvement over lemon juice but neither lemon juice nor citric acid were as good as acetic acid.

Fifth.—With samples containing *mustard* and vinegar the discoloration was much greater than with vinegar only.

Sixth.—Pepper and paprika were found to exert a darkening effect. Of these two, paprika was the most noticeable.

Summing up we would say that some benefit could be secured by substituting acetic acid for vinegar; that mustard appears to be responsible for a considerable amount of darkening and to a lesser extent pepper and paprika; that a moderate amount of salt has no effect.

Just why mustard and spices present in the small amount that they are should cause such a considerable darkening is hard to explain. A possible explanation is that the powerful volatile and non-volatile oils which these substances contain act like driers on the oil and cause them to absorb more oxygen than they otherwise would and therefore cause them to darken to a greater extent. This action would be similar to that occurring when a small amount of drier (approximately 1%) is added to linseed oil in making paint. These driers (generally compounds of lead, manganese or cobalt) cause the linseed oil to absorb oxygen very rapidly, and the paint dries in about 24 hours whereas if the drier were not used, the paint would still be soft at the end of several weeks.

In considering the whole subject of discoloration, one is impressed with the fact that the changes which take place are very complex and appear to be a combination of factors rather than any one. The oxidation of the oils is one thing, however, that is fairly well established, so that in suggesting ways and means of eliminating or at least reducing discoloration, the use of non-drying oils or oils of low oxygen absorption, would be one means.

A more feasible way commercially is to fill the package quite full so that the amount of air space above the mayonnaise is reduced to a minimum, thus reducing the amount of oxygen which the oil can absorb.

Another is to seal the mayonnaise under vacuum. Samples of vacuum packed mayonnaise have been found to show an almost negligible discoloration.

And finally, the careful selection of spices and a sparing use of them and of mustard particularly should give considerable relief from discoloration.

Special Notice A. O. C. S.

The Research Associate of the Society, Miss Walker, at the Bureau of Standards, Washington, will probably be ready to standardize all red glasses January 2. Make your arrangements with A. W. Putland, Portsmouth Cotton Oil Refining Corporation, Portsmouth, Va., for dates when the glasses can be submitted to avoid unnecessary delays. The charge for each glass will be $1.50.

In connection with this matter, the Governing Board has adopted rules requiring all referee chemists to have the following certified glasses as a minimum standard set: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 3.0, 3.5, 4.0, 5.0, 6.0, 7.0, 7.6, 8.0, 9.0, 10.0, 11.0, 12.0, 16.0, 20.0, in the reds, and 1.0, 2.0, 3.0, 5.0, 10.0, 15.0, 20.0, and 35.0, in the yellows. After the necessary time for certification of the glasses has been allowed, referee certificate will be refused unless these glasses are owned by the chemist applying.

Harris Takes Over Parks-Cramer Line

Mr. John P. Harris, Chemical Engineer, of 400 N. Michigan Avenue, Chicago, Ill., who has been representing Industrial Chemical Co. in Western and Southern territory, has added to his lines the indirect oil-heating deodorizing equipment of Parks-Cramer Co. of Boston, Mass., offering the Merrill System of deodorizer heating and control. Mr. Harris will represent the Parks-Cramer Co. in the same territory which he will continue to cover for Industrial Chemical Co.