Technical Emulsions of Oils and Waxes with Water

Careful Technique and Selected Emulsifying Agents Required in Preparation of Commercial Products

By H. BENNETT*

CHEMICALLY a more or less permanent mixture of an oil, fat, wax or other water insoluble medium and water is termed an emulsion. Before an emulsion can be prepared it is necessary to introduce a third factor known as an emulsifying agent. A typical emulsifying agent is ordinary soap. A simple experiment to illustrate a typical emulsion is to place a little linseed or other oil in a bottle and then add to it some water containing some soap. On shaking vigorously the mixture becomes milky and the oil and water do not separate at once, as would be the case if the soap were not present. This experiment can be performed on a smaller scale to better illustrate this phenomenon. If a drop of oil be placed on the surface of a glass of water it will remain in one round globule. If now a little strong soap solution is poured down the side of the glass the globule will begin to spread until it covers all of the surface of the water. This is emulsification of the oil and water by means of the emulsifying agent, soap.

For technical purposes the maker of emulsions has many factors to consider. In products which are not used immediately the "life" of the emulsion is extremely important. If a commercial product will not be used for three to six months it must be so prepared that there will be no separation during this period. An emulsion which does not separate in a given length of time is referred to as a stable emulsion. Many an emulsion when freshly made lifts its maker to the zenith of exultation but shortly drops him to the nadir of despair when it separates.

While the theory of emulsions is prolific with mathematical equations and observations made during the course of pure research, the practical side of formulation as applied to the manufacturing industries has been sadly neglected in the literature.

Before proceeding with practical working formulae for producing emulsions of every day interest and use mention must be made of some of the pitfalls encountered by the maker of emulsions. Since emulsions are by nature more or less unstable every care must be taken to produce them under optimum conditions and eliminate all deleterious and disturbing factors. Once a formula is established careful note must be taken of the amounts of each ingredient used, the rate of introduction and the order of introduction of each element, the kind and rate of stirring, temperature, time, and type of mixing apparatus must be duplicated exactly or the finished emulsion will not be perfect.

For the past three years the writer has devoted considerable time toward developing methods for the production of stable emulsions, particularly of carnauba wax which is used in so many polishing preparations. All of the known emulsifying agents were tried with more or less success. Complete success was not achieved however until ammonium linoleate was tried. Because previous processes for the manufacture of ammonium linoleate were rather costly this efficient emulsifying agent was neglected. A low priced process for making ammonium linoleate was developed which enables its production at a price so low that it can be used in the lowest priced emulsions.

Since it was found that better results were gotten by using an ammonium linoleate not especially purified, one containing ammonium salts of the homologous acids of the linoleic series, the product now used is called ammonium linoleate paste which contains about 20% moisture. It is a cream or tan colored, grease-like material, soluble in water and alcohol.

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Since it is chemically a soap the usual precautions must be observed—the avoidance of acids, salts and other precipitants.

Procedure

USING proportions given in table, first dissolve the indicated amount of water in the ammonium linoleate. This is done by covering the ammonium linoleate with the required amount of water and allowing it to soak over night. Work in slowly the next day until dissolved completely. Do not attempt to dissolve in any other way or lumps will result. To this add slowly with vigorous agitation the indicated amount of oil and continue stirring until homogeneous.

The technique for making wax emulsions is similar except that heating must be resorted to. To make a wax emulsion, dissolve the ammonium linoleate paste according to the above method. Place this solution in a pot and heat to 95-98°C. Simultaneously with this procedure melt the wax in another pot and heat to 100-105°C. As soon as both solutions are at the indicated temperatures, start the high speed stirrer in the pot containing the ammonium linoleate solution in water and run in the wax in a thin stream. In order to prevent excessive evaporation of water, the pot should be covered while stirring. Stirring should be continued until the emulsification reaches the best of results. Lengthy stirring can do no harm and can do much good. At the risk of reiteration emphasis must again be placed on the temperatures indicated above. An extreme lowering of temperature will produce a grainy effect brought about by the crystallization of wax. A fast electric stirrer is essential in producing good wax emulsions.

Very often it is desired to emulsify a solid material which melts above 100° C. Since such a substance would crystallize on touching even boiling water a simple stratagem is resorted to. The solid substance is dissolved in an oil or hydrocarbon and this solution is treated just as an oil or hydrocarbon is handled. Thus a fossil resin may be dissolved in naphtha and emulsified without the use of heat. Similarly high melting water soluble substances are dissolved in the water used in the emulsion.

Beautiful colored effects are produced in many emulsions by dissolving a water soluble dye in the water used. These colors are enhanced in beauty by the milky appearance and give many novel shades and nuances of color.

Many polishing emulsions contain abrasives and pigments. Since these latter materials have a higher specific gravity than water they will tend to settle out. In order to prevent or slow up the attraction of gravity for these particles the emulsion should be made as viscous as possible. The table given below gives a number of formulae for making various emulsions. In following these formulae it may be found that in some cases slight variations in the amount of emulsifying agent used may be necessary because of natural variations in the oils, waxes etc. (It is a well known fact that all naturally occurring organic materials show periodic variations.)

FORMULAE
(All Parts by Weight)

No.	Material Emulsified	Parts	Parts of Water	Ammonium Linoleate Parts
1.	Pine Oil	90	90	10
2.	Kerosene	90	90	8
3.	Naphtha	90	100	7
4.	Benzol	90	100	7
5.	Gasoline	90	100	7
6.	Cottonseed Oil	90	90	11
7.	Linseed Oil	90	150	8
8.	Olive Oil	80	60	10
10.	Castor Oil	90	80	12
11.	Citronella	90	90	10
12.	Chinawood Oil	90	80	12
13.	Peanut Oil	90	80	12
14.	Coconut Oil	90	80	12
15.	Paraffin Wax	90	320	24
16.	Carnauba Wax	90	420	12
17.	Asphaltum	40	200	8
18.	Beeswax	90	500	12
19.	Synthetic Wax	90	500	12
20.	Ozokerite	90	400	14
21.	Montana Wax Bleached	90	560	12
22.	Turpentine	90	100	8
23.	Nitrobenzol	90	100	8
24.	Orthodichlorbenzol	90	100	8
25.	Methyl Salicylate	90	100	8

The above formulae can be lessened in cost by reducing the amount of emulsifier used. The minimum can be determined by experiment. Increasing the amount of water will give thinner emulsions.

Formula #1 is typical of ordinary type oil, furniture and automobile polish. This is often given a lemon-like odor by dissolving a little lemongrass oil or lemenone in the oil before emulsification.

Formulae #2-5 inclusive are used for cleaning printing presses and other machinery, wood-work or porcelain.

Formulae #6-14 inclusive are used as lubricants and softeners during textile manufacture; for "stuffing" or rendering leather soft and pliable; for various specialties used in many industries where the use of the oil itself is undesireable or too expensive.

Formulae #15-21 inclusive are used as polishes for furniture, automobiles and for many industrial polishing purposes. These formulae are finding increasing use for lubrication during the processing of silk and rayon.

Formulae #22 and 25 are used for liniments and cleaners. Formulae #23 and 24 are used in shoe and metal polishes.

Many adaptations of these formulae are used for divers purposes. For example the kerosene in formula #2 may be replaced by a kerosene extract of pyrethrum flowers and then serves as an excellent fly spray and insecticide.

Ammonium linoleate emulsions of fatty acids may be used for waterproofing concrete, cement and stucco by diluting these emulsions to varying degrees and mixing them in while forming or applying these structural materials. The ammonia and water gradually evaporate and the lime magnesia present in the cement and sand combine with the linoleic and other fatty acid to form an insoluble metallic soap which is water-repellent.

The bleaching of fats, oils and waxes may be consummated by forming an emulsion of the fat, oil or wax and diluting the same with a large excess of water. There is then introduced a concentrated solution of common salt. The latter causes the emulsion to break and the fat, oil or wax rises to the surface. Some of the coloring matter stays in the water and dirt and other insoluble matter settles out on standing. Then the upper layer of fat, oil or wax is drawn off and is found to be lighter in color, free from dirt and insoluble matter and often improved in odor.

Formula #8 is used in hair treatments in place of olive oil as it penetrates better and is washed out more readily. Formulae #14 and 18 are similarly used in cosmetics.

In chemical reactions where contact between a watery solution and a water insoluble material is desired resort is had to emulsification. In this way the two media are subdivided into minute particles having an extremely large surface area with the result that the reaction proceeds more rapidly and completely. For example, if we try to hydrolyze ethylene dichloride with an aqueous solution of caustic soda we see that the two liquid phases are immiscible. If, however, the ethylene dichloride is emulsified and then treated with an aqueous solution of caustic soda, under suitable conditions, hydrolysis soon starts. These emulsions for promoting synthetic reactions should be agitated violently especially in those cases where acids or salts are present. A recent adaptation of this principle concerns itself with the hydrogenation of oils. By emulsifying the oil, infinitely larger surface is exposed to the attack of the hydrogen with a resultant increase in speed and completeness of hydrogenation.

In the paint, varnish and printing ink industries various "driers" are in continual use to speed up the drying of the oil vehicle. Metallic linoleates are in great favor in many directions. Their lack of uniformity and dark color has prevented their more universal use. They can now be made absolutely uniform and of a lighter color by adding a hot solution of a metallic salt (while stirring vigorously) to a hot solution of ammonium linoleate.

In conclusion it is hoped that the above definite exemplifications of utilitarian applications of emulsion phenomena will serve as a starting point to those technicians who are continually on the look-out for improvements in process; production of novel products; or lowering of costs and fire-hazards.

Oil of Sumac

By H. P. TREVITHICK

SUMAC berries are very plentiful in the United States, particularly along the Atlantic seaboard. They are used particularly as a source for tannin, in textile dyeing and in medicine.

On extraction with petroleum ether, they yield a dark, greenish brown colored, rather viscous oil. The total oil content was 17.54%.

This oil had the following characteristics:

Moisture & Volatile Matter @ 105° C.	0.18%
Specific Gravity @ 15.5° C.	0.9256
Iodine Value (Wijs)	96.1
Saponification Value	183.2
Free Fatty Acids (Oleic)	10.7%
Acid Value	21.4
Unsaponifiable Matter (petroleum ether extract)	2.38%
Index of Refraction @ 25° C.	1.4726
Index of Refraction @ 20° C.	1.4744
Total Fatty Acids & Unsaponifiable	95.1%
Iodine Value of the Fatty Acids	96.7
Neutralization Value of Fatty Acids	193.2
Mean Molecular Weight	296.9
Titre	25.7° C

These values are quite different from those given by *Lewkowitsch,* (See Volume II, of the VI Edition, page 246).

The hardening of stearolic ethyl ester under hydrogenation is said to occur in steps, the triple bond being reduced to a double bond before any stearic acid begins to form. Harrie's ozonation method shows the absence of any shifting of the triple bond during hydrogenation. *Chem. Umschau Fette, Oele, Wachse u. Harze* 38,23-4 (1931).