An emulsion is an intimate mixture of two liquid phases, such as oil and water, in which the liquids are mutually insoluble and where either phase may be dispersed in the other. In water chemistry, two types of emulsions are commonly found, oily wastewater (oil emulsified in water or O/W emulsions) and waste oil emulsions (water emulsified in oil or W/O emulsions).

Oily waste and waste oil emulsions can usually be differentiated visually. O/W emulsion appears to be just oily, dirty water; a drop of the emulsion added to water disperses (Figure 11.1a). A W/O emulsion is usually thick and viscous; a drop of this emulsion added to water does not disperse (Figure 11.1b).

**OIL-IN-WATER EMULSIONS**

An oily waste emulsion, in which oil is dispersed in the water phase, may contain any of various types of oil in a wide range of concentrations. These oils are defined as substances that can be extracted from water by hexane, carbon tetrachloride, chloroform, or fluorocarbons. In addition to oils, typical contaminants of these emulsions may be solids, silt, metal particles, emulsifiers, cleaners, soaps, solvents, and other residues. The types of oils found in these emulsions will depend on the industry. They may be fats, lubricants, cutting fluids, heavy hydrocarbons such as tars, grease, crude oils, and diesel oils, and also light hydrocarbons including gasoline, kerosene, and jet fuel. Their concentration in the wastewater may vary from only a few parts per million to as much as 5 to 10% by volume.

A stable O/W emulsion is a colloidal system of electrically charged oil droplets surrounded by an ionic environment. Violent mixing and shearing of oily wastewater in transfer pumps disperses these minute oil droplets throughout the water. Emulsion stability is maintained by a combination of physical and chemical mechanisms. These emulsions are similar in behavior to the colloidal systems encountered in swamps (color) and rivers (silt).

One such stabilizing mechanism, ionization, is brought about by the addition of surface-active agents, such as organic materials or cleaners, which aid in maintaining a stable colloidal system. These molecules usually carry an electric charge and seek out the oil/water interface of the emulsified droplet. Here, the accumulated charges cause the emulsion to be stabilized through repulsion of the commonly charged droplets. Neutral (nonionic) surfactants can also stabilize an emulsion, since these molecules are bifunctional: one end is soluble in water, and the other end in hydrocarbon, so the molecule bridges the interface and stabilizes it.
Fine, solid particles may stabilize an emulsion if they are of correct size and abundance. In this case, stabilization occurs because the solid particles adsorbed at the oil/water interface tend to reinforce the interfacial film. The dispersed droplets cannot coalesce because of the interference or blocking effect caused by the solids (Figure 11.2).

Emulsions can also be stabilized by friction between the oil and water phases created by vigorous mechanical or physical agitation. Static electric charges developed by this action tend to collect at the oil/water interface.

An emulsifier is usually a complex molecule, often having a hydrophilic (water-loving) group at one end and a lyophilic (oil-loving) group at the other (Figure 11.3). Emulsifiers disperse oil droplets in the water phase because they have an affinity for both water and oil that enables them to overcome the natural forces of coalescence.

Most emulsifiers are surfactants having either anionic or nonionic polar groups. Petroleum sulfonates and sulfonated fatty acids are common anionic emulsifiers, and ethoxylated alkyl phenols are common nonionic emulsifiers. Examples of naturally occurring surfactants are organic sulfur compounds, various simple esters, and metal complexes. Alkaline cleaners containing surfactants

FIG. 11.2 Physical emulsion stabilization by finely divided solids, illustrated with O/W emulsion.
that emulsify free oil are present in many wastewaters. Table 11.1 lists a variety of emulsifiers for both O/W and W/O systems.

### Breaking Oil-in-Water Emulsions

Emulsions may be broken by chemical, electrolytic, or physical methods. The breaking of an emulsion is also called resolution, since the result is to separate the

<table>
<thead>
<tr>
<th>TABLE 11.1 Emulsifying Agents</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oil-in-water type</strong></td>
</tr>
<tr>
<td>1. Formation—when soaps are colloidally dispersed in water phase</td>
</tr>
<tr>
<td>2. Ionic emulsifiers</td>
</tr>
<tr>
<td>(a). Sodium, potassium soaps and sulfides</td>
</tr>
<tr>
<td>(b). Sodium naphthenes and cresylates</td>
</tr>
<tr>
<td>(c). Precipitated sulfides plus surfactants</td>
</tr>
<tr>
<td>(d). Organic amines</td>
</tr>
<tr>
<td>3. Electrolytes which favor stability</td>
</tr>
<tr>
<td>(a). Salts of univalent cations</td>
</tr>
<tr>
<td>(b). Salts of di- and trivalent cations</td>
</tr>
</tbody>
</table>
FIG. 11.4 The action of a cationic emulsion breaker in neutralizing surface charges on a colloidal oil droplet in oily wastewater.

original mixture into its parts. Chemicals are commonly used for the treatment of oily wastewaters, and are also used to enhance mechanical treatment. In breaking emulsions, the stabilizing factors must be neutralized to allow the emulsified droplets to coalesce. The accumulated electric charges on the emulsified droplet are neutralized by introducing a charge opposite to that of the droplet (Figure 11.4). Chemical emulsion breakers provide this opposite charge. The dielectric characteristics of water and oil cause emulsified oil droplets to carry negative charges. Therefore, to destabilize an oil-in-water emulsion, a cationic (positive charge) emulsion breaker should be used.

The resolution of an O/W emulsion should ideally yield an oil layer and a water layer. However, such a clear resolution is seldom achieved: there is often a scum, called a rag, at the interface where solids and neutralized emulsifier collect.

The treatment of oily wastewater is normally divided into two steps.

1. **Coagulation:** This is destruction of the emulsifying properties of the surface-active agent or neutralization of the charged oil droplet.

2. **Flocculation:** This is agglomeration of the neutralized droplets into large, separable globules.

Traditionally, sulfuric acid has been used in oily waste treatment plants as the first step in emulsion breaking. Acid converts the carboxyl ion in surfactants to carboxylic acid, allowing the oil droplets to agglomerate. Chemical coagulating agents, such as salts of iron or aluminum, can be used in place of acid, with the additional benefit that these aid in agglomeration of the oil droplets. However, the aluminum or iron forms hydroxide sludges that are difficult to dewater. Acids generally break emulsions more effectively than coagulant salts, but the resultant acidic wastewater must be neutralized after oil/water separation.
The use of organic emulsion breakers in place of alum or salts which form hydrous flocs greatly reduces sludge volume. The oil can be extracted from the sludge.

Organic demulsifiers are extremely effective emulsion breaking agents, giving more consistent results and producing better effluent quality than an inorganic program. In many treatment plants, organic emulsion breakers have replaced traditional alum treatment for exactly those reasons. In addition to yielding a better quality effluent, organic emulsion breakers often require lower dosages than a corresponding inorganic treatment. Organic emulsion breakers reduce the amount of sludge generated in a treatment program by as much as 50 to 75% (Figure 11.5).

Table 11.2 lists emulsion breakers used in both O/W and W/O treatment programs.

**TABLE 11.2** Types of Emulsion Breakers

<table>
<thead>
<tr>
<th>Main type</th>
<th>Description</th>
<th>Charge</th>
<th>Used for</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic</td>
<td>Polyvalent metal salts such as alum, AlCl₃, FeCl₃, Fe₂(SO₄)₃</td>
<td>Cationic</td>
<td>O/W</td>
</tr>
<tr>
<td></td>
<td>Mineral acids such as H₂SO₄, HCl, HNO₃</td>
<td>Cationic</td>
<td>O/W and W/O</td>
</tr>
<tr>
<td></td>
<td>Adsorbents (adding solids)—pulverized clay, lime</td>
<td>None</td>
<td>O/W</td>
</tr>
<tr>
<td>Organic</td>
<td>Polyamines, polyacrylates and their substituted copolymers</td>
<td>Cationic</td>
<td>O/W</td>
</tr>
<tr>
<td></td>
<td>Alkyl substituted benzene sulfonic acids and their salts</td>
<td>Anionic</td>
<td>W/O</td>
</tr>
<tr>
<td></td>
<td>Alkyl phenolic resins, substituted polyalcohols</td>
<td>Nonionic</td>
<td>W/O</td>
</tr>
</tbody>
</table>
Treatment Methods

Oil separation and removal can be divided into two processes, (a) gravity separation of free, nonemulsified oil, and (b) chemical treatment and separation of emulsified oil. Oily waste is typically a combination of free, nonemulsified oil; stable emulsified oil; and insoluble solids, such as grit, metal fines, carbon, paint pigments, and corrosion products. Free oil and the insoluble solids are physically removed by gravity separation using American Petroleum Institute (API) or corrugated plate interceptor (CPI) separators.

The primary function of a gravity separator is to remove free oil and settleable solids from wastewaters to enhance subsequent emulsion-breaking treatment and optimize chemical utilization, since oil and solids consume emulsion-breaking chemicals unnecessarily. Such separators cannot, of course, remove soluble impurities nor break emulsions. Gravity separators depend on density differences to provide the buoyant force that causes the droplets of free oil to rise to the surface. Theoretically, oil droplets rise linearly as predicted by Stokes' law; in practice, turbulence and short circuiting usually disturb the separation pattern.

The API separator consists of a rectangular trough or basin in which the wastewater flows horizontally while free oil rises to the surface. (See Figure 9.22.) Oil collecting on the surface is skimmed off to a recovery circuit.

The CPI separator consists of inclined packs of 12 to 48 corrugated plates mounted parallel to each other at distances of $\frac{2}{3}$ to $1\frac{1}{2}$ (1.9 to 3.8 cm). As wastewater flows between the plates, the lighter oil globules float up the incline into the concave upper corrugations where they coalesce into larger masses which move along the plates to weep holes or to the trailing edge, and then to a floating layer at the surface (Figure 11.6). A modification of this design, shown in Figure 11.7, has been found effective on oil droplets of 0.85 sp gr as small as 5 μm in diameter.

After treatment of the oily wastewater for removal of free oil and solids, emulsion-breaking chemicals are applied to destabilize the colloidal oil, and the treated stream is then subjected to a second separation process, most commonly air flotation, which has been used for many years in the treatment of industrial wastes.

![FIG. 11.6 CPI (corrugated plate interceptor) separator uses density difference between oil and water to separate free nonemulsified oil from wastewater.](image-url)
Two basic methods of air flotation are used for O/W treatment: (a) dissolved air flotation (DAF) and (b) induced, or dispersed, air flotation (IAF).

Dissolved air flotation uses pressurized water, supersaturated with air, to produce bubbles of 30 to 120 µm upon release of pressure in the separation vessel. This causes flotation of the coagulated oil, solids, or both, as the fine bubbles are incorporated in the chemically produced floc. Induced air, on the other hand, utilizes mechanical agitation to aspirate or entrain air into the water undergoing treatment, resulting in larger bubbles, up to 1000 µm in size, for attachment to the flocs to bring them to the surface as a froth.

(See Chapter 9 for discussion of air flotation devices.)
Of the two processes, dissolved air flotation has been the more prominent in the United States, particularly in the refining industry. There are three basic flow sheets for the DAF process, (a) total pressurization, (b) partial pressurization, and (c) recycle pressurization, the latter being the preferred process in about 80% of oily wastewater treatment systems. As the supersaturated recycle water meets the chemically treated raw waste stream, the release of pressure causes the air to come out of solution on nucleation sites created by colloidal, neutralized particles. The common chemical treatment program is to apply an emulsion breaking chemical to the suction side of the supply pump, with addition of an inorganic coagulant such as alum to the discharge side; a high molecular weight flocculant is applied to the recycle stream so that the floc formation occurs as the air comes out of solution on the nucleation sites.

The DAF system usually includes the following (see Figs 9.23 and 11.8):

1. The DAF flotation vessel, a rectangular or vertical cylindrical unit with baffles and skimmers.
2. Recycle hardware, including the recycle pump, air compressor, and saturation tank.
3. Rapid mix and flocculation devices where required as a separate entity because of low temperature (slowing floc formation and separation velocity), fragile floc, or both.

As with the DAF unit, froth formation is produced in the IAF unit by chemical treatments normally added to the influent. The treated waste sometimes goes
through a static mixer to hasten reaction and allow floe to form in the first cell of the series. The treatment scheme is different because the IAF depends on adherence of impurities to the bubble surface. Because the IAF can be designed to operate at higher hydraulic loading than DAF units, the larger bubbles rise faster. These units are often selected because of space savings and lower installed cost. Table 11.3 compares some of the performance characteristics of IAF and DAF units in oily waste treatment.

Induced air flotation systems usually have a lower installed cost per unit of throughput compared to DAF units. However, as the table shows, this is achieved at the expense of effluent clarity and collected sludge density. However, there are many applications where scaling the bulk of oil and solids is the major goal, as in side-stream treatment of recirculating cooling water in rolling mills, where the presence of some oil is acceptable, but a certain volume must be continuously removed to stay within acceptable limits in the bulk of the recirculated water.

Ultrafiltration consists of forcing an oily emulsion to pass through very small pores (less than 0.005 μm) in a membrane. Only water and dissolved low molecular weight materials can pass through the pore structure of the membrane, leaving a concentrate of the emulsified oil droplets and suspended particles. Plugging does not occur as it can in ordinary filtration because particulates are much larger than the pores and cannot enter the membrane structure.

Activated carbon adsorption has been used to clean up wastewater containing lesser amounts of soluble and emulsified organic contaminants (less than 100 mg/L). This is usually employed as a polishing step.

Coalescers are used where oily water may contain free oil and oil in a weakly emulsified state; examples are tanker ballast and oil field brines. There are a variety of designs, ranging from simple, baffled vessels where coalescence is induced by eddy currents, to rather sophisticated devices using membranes which allow water to pass through but reject oil. Coalescing devices for treating oily water, such as oil-contaminated condensate, include terry-cloth filters (a variety of cartridge filter) and coarse sand pressure filters. Of course, the coalescer by itself is

<table>
<thead>
<tr>
<th>TABLE 11.3 Comparison of DAF and IAF Flotation Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved air flotation</td>
</tr>
<tr>
<td>1. Air is dissolved into water. Air saturation equipment is required.</td>
</tr>
<tr>
<td>2. Flotation of impurities due to bubbles enmeshed into flocs of solids and oil.</td>
</tr>
<tr>
<td>3. Air bubble size of 30–120 μm produces slow rise rate.</td>
</tr>
<tr>
<td>4. Lower loading rates because particles rise slower; longer detention time.</td>
</tr>
<tr>
<td>5. Low turbulence and longer detention time reduces floc carrythrough.</td>
</tr>
<tr>
<td>6. Chemical program focuses on coagulation and flocculation.</td>
</tr>
<tr>
<td>7. Higher density of solids and oil in skimmed float.</td>
</tr>
</tbody>
</table>
seldom adequate; it must be followed by a gravity separator or a filter, as is used in the treatment of oily condensate.

**WATER-IN-OIL EMULSIONS**

Water-in-oil emulsions are viscous, concentrated substances formed when oil comes into contact with water and solids. Metal particles and other solids may be coated with surfactants in such a manner that they are preferentially wetted by the oil rather than the water (Figure 11.9). In circumstances where agitation is present, the water becomes dispersed in the oil as a fine emulsion, and these small water droplets together with the oil-coated solids maintain the stability of the emulsion. Many types of water-in-oil or waste oil emulsions are found. Table 11.4 classifies some of the more common waste oils according to their relative oil, water, and solids content.

**TABLE 11.4 Classification of Waste Oils**

<table>
<thead>
<tr>
<th></th>
<th>Percent oil</th>
<th>Percent water</th>
<th>Percent solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refining—crude</td>
<td>90–95</td>
<td>5–10</td>
<td>0–5</td>
</tr>
<tr>
<td>Machining—cutting, grinding oil</td>
<td>50–80</td>
<td>20–50</td>
<td>0–20</td>
</tr>
<tr>
<td>Waste treatment sludges</td>
<td>40–50</td>
<td>40–50</td>
<td>5–10</td>
</tr>
<tr>
<td>Steel mills—rolling oils</td>
<td>80–95</td>
<td>5–20</td>
<td>0–5</td>
</tr>
</tbody>
</table>

**W/O Emulsion Stabilizers**

Among commonly occurring substances that promote or stabilize W/O emulsions are soaps, sulfonated oils, asphaltic residues, waxes, salt, finely divided coke, sulfides, and mercaptans. Finely divided solids varying in size from colloidal to 100 μm and larger are particularly effective in stabilizing these emulsions.
The presence of hydrophobic and hydrophilic colloidal solids at the oil/water interface may result in the larger particles aggregating around the dispersed droplets. The presence of these large particles throughout the continuous phase tends to form a complex matrix consisting of solids, oil-in-water, and water-in-oil emulsions existing simultaneously as a stable mixture in which either oil or water may be the continuous phase.

**Breaking Water-in-Oil Emulsions**

Water-in-oil emulsions can be broken by chemical or physical methods, including heating, centrifugation, and vacuum precoat filtration. Centrifugation breaks oil emulsions by separating the oil and water phases under the influence of centrifugal force (Figure 11.10). Filtration of waste oil emulsions can be accomplished through high rate sand filters (HRF) or diatomaceous earth (DE) filters (Figure 11.11). The operation of these pieces of equipment must be carefully controlled to provide the highest quality of upgraded oil.

Chemical treatment of a waste oil emulsion is directed toward destabilizing the dispersed water droplets and solids or destroying emulsifying agents. Acidification may be effective in breaking W/O emulsions if the acid dissolves some of the solid materials and thus reduces surface tension.

The newest method involves treatment of a W/O emulsion with a demulsifying agent containing both hydrophobic and hydrophilic groups that is able to form a water wettable adsorption complex. The mechanism of W/O emulsion breaking can be best explained by visualizing the displacement of the original emulsifying agent from the interface by a more surface-active demulsifying material. This process can be enhanced by heating to reduce viscosity and increase the solubility and rate of diffusion of the emulsifying agent in the oil phase. Because water droplets in oil tend to be positively charged, these types of emulsions are typically treated with an anionic (negative charge) organic emulsion breaker. Sometimes a combination of acid and organic demulsifying agent provides the best results.
In all cases, the treatment reagents must be thoroughly mixed into the W/O emulsion to provide intimate contact with the emulsified water droplets. Heating the emulsion to 120 to 180°F (49 to 82°C) often produces rapid separation. Adequate settling time must be allowed to provide for optimum resolution of the oil, water, and solids phases (Figure 11.12).
INDUSTRIAL SOURCES OF EMULSIONS AND TREATMENT PRACTICES

An industrial activity that requires the use of process oils and water may be susceptible to emulsion formation at any point in its system. The three major industries producing oily waste are petroleum refining, metals manufacturing and machining, and food processing.

Hydrocarbon Processing Industry

Petroleum refining operations generate both O/W and W/O emulsions, present in drainage water, spills, separator skimmings, tank bottoms, and various oil recovery traps.

In the petrochemical industry quench waters generated in ethylene and other olefin manufacturing operations may contain mixtures of heavy, middle, and light hydrocarbons.

In the processing of crude oil, desalting is used initially to remove corrosive salts carried by the oil. In desalting, water is mixed with crude oil to wash it free of these salts. This forms a water-in-oil emulsion that is resolved in an electrostatic device, usually assisted by demulsifying chemicals. Frequently, however, not all of the emulsion is resolved, and the residue must be separated for further treatment. Often this emulsion is dumped into an oily sewer along with O/W and W/O emulsions formed in crude fractionation, thermal cracking, catalytic cracking, and other processes. All of these emulsions contain too much water to justify processing, so they are usually dumped into an oily sewer system.

In the oily sewer, these emulsions are stabilized. Oil spills from process and general oil runoff are sent to this sewer along with oily wastewater, storm water, dirt, and debris. These components are mixed by pumps and flow turbulence in the sewer to form additional emulsions, or to further stabilize those already formed. The oils making up these emulsions are typically mixtures of light and heavy hydrocarbons.

The oily wastewaters collected from various points throughout the plant are delivered in a sewage system to an API separator. The skimmings from the API separator, which are usually good oil with low levels of solids and water present, may be sent back to the desalter or the coker. The underflow from the separator goes on to dissolved air flotation units (DAF). The underflow (the water) from the DAF unit may flow to a bio-oxidation pond and then to a clarifier before the water is ultimately sent to a river or sewer system (Figure 11.13). Emulsifying agents are not usually found in these O/W emulsions.

Waste oil treatment in refineries may be concerned with two different types of sludges or emulsions: skimmings from the API separator and the DAF units are typically sent to an oily sludge holding tank; the second type of waste oil emulsion in a refinery, leakage from processes, is often collected in various types of traps and drains throughout the plant. This oil may be of high enough quality that it can be blended with crude feedstock and returned to a process desalter or the coker unit.

A common measure of oil quality is the percent bottom sediment and water (BS&W). (Crude feed to a desalter typically has no greater than 5% BS&W.) If the reclaimed oil quality is too poor for use as desalter feed blend, the emulsion may
be stored in a separate container or may be mixed with the API and DAF skimmings. These tanks typically have heating and recirculation or other type of mixing capabilities. Often, the fugitive waste oil emulsions can be separated solely by heat and a quiescent settling period. The API and DAF skimmings typically do not respond to this treatment, requiring the addition of a chemical W/O emulsion breaker. In either case, emulsion breakers can be used to effect a more rapid, complete separation of the oil, water, and solids phases. Treatment with an organic emulsion breaker involves feeding the chemical to the line while the treatment tank is filled. This is followed by a quiescent period ranging from one to several days. The separated layers can then be drained. The solids which are not oil-wet can be trucked to an approved landfill. The water, which may contain residual emulsified oil, is recycled back to the head of the oily wastewater treatment system and the recovered oil may be used according to individual plant needs.

Basic Metals Industry

Oily wastes generated in steel mills include both emulsified and nonemulsified, or floating, oils. Oily wastes from hot rolling mills contain primarily lubricating and hydraulic pressure fluids. Wastes from cold strip operations contain rolling oils that were used to lubricate the steel sheet and reduce rust. Oil-in-water emulsions are sprayed on the metal during rolling to act as coolants.

Wastewaters from these plants typically have a wide variety of contaminants, and the objectives of treatment include removal of not only oil, but also solids and metal fines. In a typical steel mill waste treatment scheme (Figure 11.14), the
plant wastewater enters an equalization tank, where the detention time is a few hours. The water then flows to an air flotation unit, where it may be treated with organic or inorganic coagulants. The skimmings from the flotation unit may be pumped to a storage tank for batch treatment with waste oil emulsion breakers. The underflow from the flotation unit usually passes to further treatment or is recycled.

Waste oil treatment in the primary metal industry is usually more complicated than in a refinery. Chemical emulsion breaking treatment programs often require the addition of acid to dissolve metal fines. In batch treating these emulsions, it is important that the chemical be thoroughly mixed into the emulsion and that heat be applied throughout the treatment and settling stages. After the settling period, the solids and water layers can be disposed of in the same way that refinery rag layers are handled. The oil layer is high quality and may be suitable for use as a boiler fuel blend or may be sold to a re-refiner or oil reclaimer.

**Automotive and Machining Industries**

Metalworking and metal parts manufacturing plants generate waste streams containing lubricating and cutting oils, lapping and deburring compounds, and grinding and other specialty fluids.

The wastewater generated in these plants contains a wide variety of oils and surfactants, so may require complicated treatment. The wastewater from several different operations often arrives at the treatment plant in separate streams or may be blended in the sewer system (Figure 11.15). All wastes flow to an equalization tank and then through several chemical feed and mix tanks prior to entering a flotation unit. The flotation skimmings are collected in storage tanks and

<table>
<thead>
<tr>
<th>Chemical addition</th>
<th>Skim oil</th>
<th>Separated water</th>
</tr>
</thead>
<tbody>
<tr>
<td>20,000 gal separator tank</td>
<td>800 gal oil tank</td>
<td>To boiler as fuel</td>
</tr>
</tbody>
</table>

**FIG. 11.14** Typical oil recovery/oily waste treatment plant in a steel mill.
FIG. 11.15 Automotive waste treatment flow sheet, typical of engine and machined parts operation.

the underflow from the air flotation unit may then pass to final treatment or recycle.

The flotation skimmings can be pumped to lead-lined cooking tanks where they are treated with acid, an organic waste oil emulsion breaker, and a high molecular weight polymer for oil recovery. The rag layer from this treatment is sold to an oil scavenger and the good, recovered oil may be burned as boiler fuel or reused in various plant processes.

Meat and Food Processing

Rendering plants, creameries, bakeries, breweries, and canneries generate emulsions containing natural fats and oils from animal processing and oils from packing and container manufacture. Both of these operations occur on the same premises, and the waste streams may be mixed.

Textiles

Wastewaters from cotton and wool manufacturing plants contain oils and greases from the scouring, desizing, and finishing operations. Oily wastewater in the synthetic fibers industry is produced during desizing and scouring. Finishing oils are used to reduce friction and snagging of fibers on spinning machines. These types of oils may also be associated with machine lubricating oils in the plant oily wastewater.
Miscellaneous Industries

Many other industries have processes which may generate oil or oily wastewater such as paints, surface coatings, and adhesives; oils, fats and waxes; soaps and detergents; dyes and inks; and certain processes of the leather industry. All have potential emulsion problems that can be solved by one or more emulsion-breaking techniques.

**RECOVERY OF SEPARATED OIL**

Whether the oil separated from waste had originally been present as the continuous or the dispersed phase, a final step is required to segregate this oil fraction and recover its value as fuel or product.

Overflow skimmers, sometimes simply a horizontal pipe with a wide slot cut lengthwise in the top that can be rotated until the slot is partially submerged, are commonly used in API and CPI separators. Inevitably, some water is withdrawn with the oil; the skimmings are drained to a manometer-type separator (Figure 11.16) and the oil fraction is separated for recovery. An alternative is to use a mechanical separation device comprising a continuous belt or tubing partially immersed in the floating oil layer; the belt or tubing is fabricated of a material that is selectively oil-wetted, so its surface becomes coated with oil that is then removed by a doctor blade into an oil receiver (Figure 11.17).

![Manometer-type oil-water separator](image-url)

**FIG. 11.16** Manometer-type oil-water separator $\Delta L$ based on the difference between specific gravity of oil and specific gravity of water.
FIG. 11.17 Free oil is often collected from water surfaces in a separation tank by means of an endless belt or loop made of oil-wettabl plastic. (Courtesy of Oil Skimmers Inc.)

If the oil emulsion has been broken by heavy chemical treatment, especially if a coagulant like alum has been used, the oily product is pastelike in consistency and requires additional chemical treatment to free the oil for recovery. Although hot acid treatment alone has been successfully used for this, special corrosion-resistant equipment and protective devices for personnel are required. High-temperature reaction with organic surface-active reagents at a controlled pH has been used as an economical replacement for strong acid treatment. In some cases, the plant having this problem has an incinerator for other wastes, and the heating value of the pastelike oily matter will support combustion and allow it to be burned in the incinerator despite the presence of chemical conditioners and imbibed water.