Wastewater from machining and casting operations contains a stew of fluids, including hydraulic oils, die lubricants, mould release agents, cutting fluids, coolants and cleaning agents. It has a milky or cloudy appearance and a high concentration of animal and vegetable oil, as well as mineral oil and grease (MOG), after free oil removal. Samples of chemically stabilized oil-emulsified wastewater are shown in Figure 1.

Emulsified oils can be generated mechanically and chemically. Mechanical emulsification is induced by agitation from pumping or mixing. This type of emulsion is relatively unstable and will exist for a relatively short time, allowing for conventional gravity separation to be used for removing the emulsion.

Knowing whether the oil-emulsified wastewater contains an unstable emulsion is helpful when deciding how to treat it. A simple method for determining an unstable emulsion is to heat a sample volume of the wastewater in a jar with warm water to approximately 70°C. If separation occurs, that means the thermal energy has increased the buoyancy of the emulsion, allowing for separation. Another approach is to cool the sample on ice to increase density difference; the emulsion may float to the surface.

If either of these methods results in the oils and greases being separated, then conventional gravity separation can usually be applied. Otherwise, the oil emulsion is chemically stable and an alternative pretreatment approach will be required.

Impact of chemically emulsified oil on wastewater

The colour of oil-emulsified wastewater can be explained by the Tyndall effect (scattering). Visible light being scattered off the suspended “oil droplets” or micelles generates a unique colour or appearance. A cloudy or milky-looking appearance indicates that the diameter of the micelles is 1 µm or greater.

The micelles can be generated by detergents and surfactants, reducing the surface tension in the solution, which allows for the formation of the micelles. Some examples of surfactants are stearic acid, laurel dodecyl sulphate, alkanol amide and sodium sulphonate fatty acid salt. These chemicals generate a stable emulsion due to their chemical structure, which has two opposing ends. One is hydrophobic (water-fearing) and the other is hydrophilic (water-liking).

The surfactant is contained in the outer surface layer of the micelle, with the entangled hydrophobic ends directed to the interior of the micelle. The hydrophilic ends directed into the aqueous phase allow for the micelle to be a stable suspension in water. The interior of the micelle is a suitable environment for organics and particulates. This results in a relatively high concentration of organics and particulates suspended in the wastewater. Possible consequences of this are wastewater quality parameters that exceed acceptable sewer discharge by-law limits.

Lubricants contain oils that generally constitute 60% to 80% of the mixture. The remainder are chemicals that constitute the additive package. The additive package may contain detergents (surfactants) that aid as friction modifiers and reduce oil deposits (or sludge), viscosity modifiers, anti-foam agents, and dispersants, pour-point depressants that disrupt crystal formation of any waxes, extreme pressure agents and anti-wear compounds.

Water-soluble cutting fluids are generally mineral, animal and vegetable oils blended with surfactants and then diluted to a concentration of 5% to 10% in water. Some cutting fluids may appear to be clear, while still containing oils and surfactants. Cooling fluids can also contain polyethylene glycol (PEG). Cleaning agents applied on the manufacturing floor may contain chemical detergents.

How do all of these chemicals contribute to exceedances in sanitary sewer discharge by-law limits.
by-law quality limits? Chemically stable micelles can be generated by the detergents and surfactants utilized as friction modifiers, dispersants, cutting fluid additives and cleaning agents. The biochemical oxygen demand (BOD), chemical oxygen demand (COD), fats oil and grease (FOG) and MOG are affected by the oils and greases in the lubricating fluids. Levels of zinc, phosphates and sulphur are affected by zinc dithio diphasate esters (ZDDP), acid phosphates and sulphurized fats, respectively, that are utilized as anti-wear and extreme pressure agents.

Styrene, aromatic compounds and phenol content in the wastewater can be affected by the styrene esters, alkylene coupled aromatic compounds, and coupled alkyl phenols, respectively, applied as pour-point depressants. Total suspended solids (TSS) of the wastewater can be affected by dirt, rubber and metal particulates or fragments that may be encapsulated by the surfactants. These encapsulated particles provide additional surface area where oils or chemical agents can reside.

Thus, potential chemical contributors to the exceedances in the sewer by-law limits are chemicals from the fluids and lubricants that make up a necessary part of the manufacturing process.

**Total suspended solids (TSS) of the wastewater can be affected by dirt, rubber and metal particulates or fragments.**

**Pretreatment technologies**

Typical approaches to dealing with chemically stable oil-emulsified wastewater, after free oil removal, include:

- Chemical treatment with coagulating and flocculating agents in a dissolved (DAF) or induced (IAF) air flotation system.
- Concentration of the emulsion by evaporation.
- Concentration of the emulsion by ultrafiltration.
- Chemical treatment with coagulating and flocculating agents in a dissolved (DAF) or induced (IAF) air flotation system.
- Concentration of the emulsion by ultrafiltration.
- Concentration of the emulsion by evaporation.

**Coagulation and flocculation**

Coagulating reagents generally destabilize the suspension of micelles, by reducing the double layer surrounding the charged surface of the micelle, or neutralizing the charges in the double layer. Reduction in the double layer thickness allows for closer contact of the micelles. Flocculating agents entrap the bridged micelles in the sweep floc, generating the organic float (frothy suspension).

Organic float that is generated by flocculation can be skimmed off the surface of the wastewater. It usually constitutes 5% to 10% of wastewater volume being treated. It can be dewatered by a filter press and roughly 10% of the float volume will be generated as pressed organics.

Filtrate from the press is returned to the treatment process. The aqueous phase from the DAF unit contains watersoluble organics that can contribute to the BOD. Therefore, this phase may require additional treatment to meet local sanitary sewer by-law limits. Otherwise, surcharges will need to be included in the operating costs.

continued overleaf...
DAF and IAF systems increase buoyancy of the flocs that are generated by the coagulating and flocculating agents. This is achieved in the DAF system by pressurizing, with air, a portion of the aqueous effluent that is sent back to the DAF tank. The flocs in the DAF tank are nucleation sites for the dissolved air to go out of solution, which subsequently provides increased buoyancy for the flocs.

In the IAF system, a sparger is applied in the tank to generate air bubbles in the wastewater. These air bubbles prefer to attach to a surface such as the flocs, which increases the buoyancy of the flocs.

Wastewater may require pH adjustment prior to addition of the coagulating and flocculating agents as these agents have a pH range over which they are effective. Increasing pH can also aid in precipitating dissolved metals in the wastewater.

The effectiveness of the coagulant and flocculant is influenced by chemicals in the lubricants, because different detergents and dispersants can generate more stable micelles. The chemical reagents and/or concentration applied may require modification if changes occur in fluids used in the plant, since they subsequently end up in the process wastewater.

Ultrafiltration

Ultrafiltration (UF) is an approach that may physically retain the micelles, with water removal of up to 90% or greater being achieved. Materials of membrane construction can be polymeric, ceramic or metal-based. The membrane structure can be a composite or an asymmetric homogeneous material. Membrane material and manufacturing process influence average pore size, pore size distribution, and porosity of the UF membrane.

UF membranes are described by average molecular weight cut-off (MWCO), expressed in units of Daltons. The average MWCO corresponds to an average pore size. The pore size range for UF membranes is 0.01 to 0.1 µm, with an approximate MWCO of 10,000 to 100,000 Daltons, respectively.

As noted previously, the diameter of the micelles in the milky wastewater is approximately 1 µm or greater. Therefore, a UF membrane with a pore size significantly less than the diameter of the micelles can be applied to retain the micelles. The UF membrane cannot retain water-soluble organics of molecular weight less than the UF membrane MWCO.

The micelles can reversibly and irreversibly foul the UF membrane pores. Tubular UF membranes are usually applied in these applications instead of spiral-wound or hollow fibre. The relatively high influent flow, that can be applied in tubular membranes, generates turbulent flow radially and axially, which induces mixing. Further, the surface eddies generated aid in reducing the cake layer and membrane fouling. To achieve high recirculation flows, the UF system utilizes relatively large pumps and piping. Membrane life is affected by membrane materials, chemicals present in the wastewater, and cleaning frequency.

Pre-filters are required upstream of the UF system to remove emulsified particulates. Generally, filter screens of mesh smaller than 100 µm are applied in the pre-filter. Pre-filters add to operating cost of the process.

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tional costs of the UF system, as they can be spent in a relatively short time due to the emulsified particulates. The cost of pre-filter replacement and disposal of the spent pre-filters must be considered when establishing operating costs. The permeate stream may require additional treatment, due to water-soluble organics with a molecular weight less than the MWCO of the membrane. Otherwise, surcharges will need to be considered in the operating costs.

The ability to restore a fouled UF membrane depends on the cleaning treatment that can be applied. The maximum operating temperature of some polymeric membranes can be 60°C. Some chemicals, such as glycols and silicones, can also irreversibly foul polymeric membranes. Ceramic and metallic membranes, which have a relatively broad range of tolerance to operating temperature and solvents, are viable alternatives.

**Evaporation**

Evaporation-based technology has been successful in concentrating oil-emulsified wastewater with water removal of 90% or greater being achieved. Evaporation by mechanical vapour recompression (MVR) is less energy-intensive than atmospheric evaporation. MVR accomplishes this by recompressing vapours from the evaporator to a higher pressure to condense them in a heat exchanger. Latent heat energy of the condensing vapours is transferred to the recirculating bottoms in the evaporator. Improved heat energy utilization is obtained by an additional heat exchanger, that is applied to preheat the feed with the higher enthalpy of the condensed distillate.

Lubricants can contain low boiling point organics, which can be present in the distillate. Therefore, the distillate may require additional treatment to remove low molecular weight organics or the surcharge costs can be applied to the operating budget. If the evaporation system can utilize waste heat from processes within the manufacturing plant, such as furnace exhaust for heat treatment, there may be reductions in overall operating costs.

MVR systems require regularly scheduled cleaning, due to the presence of organics in the wastewater that can foul the heat transfer surfaces. The compressor also requires maintenance. The MVR system will require alloy metals for piping and components if corrosive chemicals are present in the wastewater. Operating costs for residual dewatering and removal will also need to be considered.

**Conclusion**

The type of treatment selected for handling an emulsified oily wastewater will depend on many factors. These include available plant footprint, allowable capital expenditure, personnel available with appropriate skills to operate the equipment, future demands on the treatment process, and required downstream processing to provide an acceptable effluent that can be discharged. Each manufacturing plant is unique and so are its wastewater treatment issues. A cost-effective and robust solution can be achieved by performing a brief cost analysis of potential pretreatment solutions.

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