

HANDLING OF SPENT OIL-BASED PRODUCTS IN THE MECHANICAL ENGINEERING INDUSTRY

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ABSTRACT

Different aspects are reviewed of the management of emulsified petroleum products in mechanical engineering industries with reference to the waste problem. Poor quality of make-up water, poor hygienic conditions, inadequate design of feed systems and failure to use a suitable bactericide influence the volume that has to be discarded and then subjected to waste treatment. The inadequacy of the feed systems is particularly striking in many instances. Different physical and chemical methods for treatment of wasted emulsions are described. Attention is also given to laboratory procedures for the evaluation of these methods. A respirometric technique for examining the compatibility of treated wastes with sewage treatment is described.

INTRODUCTION

It is now well recognized that the discharge of untreated oil-containing waste waters to lakes or streams or to sewage works is incompatible with modern water pollution control.

Formulated products derived from oil find extensive use within the mechanical engineering industry, in operations such as cutting, drilling, grinding, etc. Their primary function is to lubricate and cool in order to increase the rate of manufacture, to reduce the wear of tools and to improve the surface properties of the manufactured articles. The collective term most commonly used is 'cutting fluids' but 'coolants' or 'lubricants' are used as synonyms.

Cutting fluids are of three basic types: straight oils, oil-in-water emulsions, and soluble oils. The term soluble oil is currently used but is inadequate from a terminological point of view. This paper will deal mainly with the problems relating to the disposal of spent cutting fluids of the emulsion type. The straight oils will not appear in the waste water system, except by accident. The waste waters obtained from wet-degreasing operations give rise to similar problems and will be referred to when appropriate.

Cutting fluids of the emulsion type are purchased as concentrates and are diluted with water before use. The concentration may vary from 0.5 to 5 per cent depending on the type of use. The normal interval seems to be 1-3 per cent. The basic constituents are an oil and an emulsifier. The oil may be petrochemically derived or a fatty material. The emulsifier is usually an

anionic surfactant of the sulphonate type. The concentrates also contain corrosion inhibitors, still largely nitrite, although other types are slowly taking over, and materials designed to improve the performance at extreme pressures and temperatures (EP additives). Bactericides are usually added to prevent microbial deterioration.

The number of marketed products is extremely large. It is not unusual for a manufacturer to claim that he can satisfy the particular demands of each manufacturing operation with a specialised formulation. This will create considerable difficulties for the average customer when, with his limited or non-existent means of testing the performance of an offered product by objective methods, he wishes to make a wise and sensible choice of cutting fluids for his shop.

This paper is partly based on the work carried out by an *ad hoc* group organized under the auspices of the Swedish Association of Metalworking Industries. The work done within this group may be considered as a joint effort of the National Environment Protection Board, the mechanical engineering industry and our Institute. Manufacturers of cutting fluids have also participated. The object was to identify the problems relating to the handling of spent cutting fluids and, once the problems had been identified and properly analysed, to issue recommendations for the industry concerned, for the local and regional authorities, and for the product manufacturers.

THE PROBLEMS

The principal concern over spent cutting fluids relates to their interference in various ways with the biological systems of lakes, streams and sewage works. The oil content may further impair the quality of waters with respect to their fitness for potable use. As a result, the handling of oil-containing wastes such as spent cutting fluids is subject to local or general restrictions in many countries. The restrictions have mostly been given the form of effluent or stream standards, which seem sometimes to be based on fairly arbitrary considerations.

A standard does not solve a pollution problem. If a standard for oil content of effluents is to be prescribed, in spite of the obvious shortcomings of standards of this kind, and if it is to be more than an empty figure, it has to be combined with a careful analysis of what is required for its implementation. Not only must the existing technology be considered, but also a number of purely practical problems. An existing need for research, development and organisation must be satisfied in many cases before a standard can be given a shape which takes proper account of the performance, cost and practicability of any pollution control measures needed.

There are two different ways principally to prevent water pollution by spent cutting fluids. One is to evaporate and burn the fluids in a special type of furnace, and the other is to separate the oil from the water by efficient physico-chemical methods. If the separation can be made satisfactorily complete, it might be desirable to subject the water—which may have a BOD₇ of from *c.* 150 ppm and upwards—to some kind of biological treatment, e.g. in a municipal sewage works, in order to degrade the residual dissolved organics.

The evaporation–burning technique may of course be characterized as a complete solution—at least as far as water pollution is concerned. The available information indicates that it is comparatively costly, however, and it will therefore be mentioned only briefly.

To separate the oil from the water, the emulsion must first be made unstable by the addition of a suitable chemical agent. Simultaneous adjustment of the physical conditions (temperature, field of gravity) may also be necessary¹. Separation of this kind would appear to be a very simple problem. A number of purely practical factors complicate the situation appreciably, however. These, as summarized below, must be given thorough consideration when the desired recommendations or standards are to be established:

(1) The waste treatment technology relating to spent emulsions differs widely in character from the manufacturing technology of the industry concerned. Fully competent personnel may therefore not be available except in the very large units. At least the smaller companies, furthermore, may prefer to use nothing but cheap, unqualified labour for the handling of this kind of waste—unless they are advised against it with the proper authority.

(2) The industrial enterprise may be anything from a small workshop with a dozen machines specializing in mass production of a few, simple articles up to the largest car factories. The merits of both simple batch procedures and more sophisticated continuous treatment processes have therefore to be evaluated.

(3) It has been found that different types of emulsions may require different combinations of chemicals if a satisfactory separation is to be achieved in all instances. It is not uncommon that a single manufacturing unit uses a large number of different brands of cutting fluids, some of which may not be compatible with the same kind of treatment. Any choice of method or of chemicals for their treatment must therefore be preceded by practical testing. Most factories lack the equipment, personnel and experience required for such testing.

(4) There will always be practical difficulties in making sure that instructions based on recommendations concerning the handling of wastes are satisfactorily observed. There is indeed a considerable risk that such instructions are disobeyed whenever it is convenient to do so. Instructions have therefore to be combined with a system of information and promotion directed to the people on the workshop floor. Furthermore, fairly uncomplicated and easily handled procedures may have to be accepted for use in small enterprises in order to make compliance with instructions more attractive. Finally, any requirements for treating the effluents will have little meaning unless proper facilities are organized to enable the industry to dispose of the oil sludge formed in most treatment processes.

MANAGEMENT OF CUTTING FLUIDS

The basic principle for waste water treatment is that all means for reducing the volume of the waste requiring treatment should be explored carefully and in an unprejudiced manner. The proper application of this principle to spent cutting fluids would start with an analysis of all factors which

may speed up their deterioration and thus increase the number of batches which have to be discarded.

Deterioration by microbial attack is probably the predominant reason for discarding a batch of cutting fluid. This is not unexpected, as these materials may be very good substrates for certain bacteria. This has in fact been accentuated in recent years when the markets in most countries have switched from biologically stable to easily biodegradable (easily attacked by bacteria) surfactants, including emulsifiers, either by voluntary agreement or by legislation. The bacterial attack on an emulsion may cause it to split, and this is favoured by the presence of certain nutrients. The effect seems to be more adverse when anaerobic (oxygen-free) conditions are allowed to develop. 'Monday odour' is a manifest sign of anaerobic conditions. The bacterial degradation of cutting fluids may be a result of one or more of four principal factors: poor quality of make-up water; poor hygiene around the machine; inadequate design of the feed system; failure to use a suitable bactericide.

The quality of the make-up water is not unimportant. A poor water coming from a polluted river or well may introduce certain nutrients which will promote the growth of bacteria. A minimum requirement is, therefore, that tap water is used for make-up unless a surface water or well of very good quality is available. Tap water may have definite disadvantages in some situations, however. It normally contains some sulphate which will be reduced to sulphide in systems prone to develop anaerobic conditions. The sulphide ion has a sickening odour and is corrosive. The corrosivity is enhanced by organic acids which are formed simultaneously. The presence of sulphide under anaerobic conditions gives rise also to a process which is probably electrochemical in which sulphide ion and iron fines react to form ferrous sulphide. This will give an unsightly bluish colour to the emulsion, indicating an unacceptable state of affairs. Furthermore, the tap water in hard water areas is characterized by undesirably high levels of calcium and magnesium, which tend to become even higher due to the appreciable evaporation which takes place in certain manufacturing operations. This will have a destabilizing effect on the emulsion and may, in addition, give rise to the formation of scales. Shops with the problem of bad odours, and having a hard water supply, are recommended to discuss possible remedies with their supplier of cutting fluids.

Phosphate is the most important nutrient involved in the bacterial decay of cutting fluids. It has been reported that the feed systems may contain much higher levels of this nutrient than would be accounted for by the make-up water. This phenomenon indicates, bluntly speaking, that the machine is placed at an inconveniently long distance from the nearest toilet. A further cause of high phosphate levels may be poor rinsing after cleaning-out operations in which detergents based on polyphosphates have been used. Such detergents should be avoided on principle.

Poor design of the feed system seems to be the most common reason for premature bacterial decay of a cutting fluid. A chemical engineer would undoubtedly characterise the traditional feed systems as being designed with complete indifference to all the factors which favour bacterial attack on the content. The machine designers must in fact be made more aware

that the consumption, and thus the not insignificant cost, of cutting fluids is highly dependent on design factors.

The feed systems should be capable of serving three main functions: transporting the cutting fluid to and distributing it on the tool and the work-piece and returning the drippings to the storage tank; offering adequate conditions for storing a suitable volume of fluid so that replenishment is not required too often; providing facilities for the removal of scraps and fines emanating from the tools and work-pieces. The first function is directly related to the production and therefore well taken care of. The incorporation of the two other functions into a suitable system seems, on the other hand, to have been a less inspiring task for the design engineers.

Feed systems may belong to one of three categories: systems serving a single machine; systems serving a limited number of machines; systems serving a large sector of the production from a central, specially designed unit placed separately from the workshop proper.

Machine tools are by tradition constructed with an internal tank for the cutting fluid placed in the foundation. Nooks and corners of such tanks form dead ends with respect to the circulation of the contained fluid. This will promote anaerobic conditions, and consequent bad odours and decay. The small tank volume, furthermore, provides an insufficient detention time for proper removal of fine solids. The circulating fluid may then run with too high a content of solids, which impairs its quality from the production point of view. The deposits formed in the tank will be difficult to remove completely; the dregs will readily turn sour and act as pools of anaerobic organisms. The cleaning-out necessary when a batch has had to be discarded because of bacterial decay is difficult, as is the succeeding inspection to determine the efficiency of the operation. It seems therefore justifiable to classify feed systems based on internal tanks as technically inappropriate. Replacement by tanks separate from the machines is strongly recommended. A simple design is suggested in *Figure 1*.

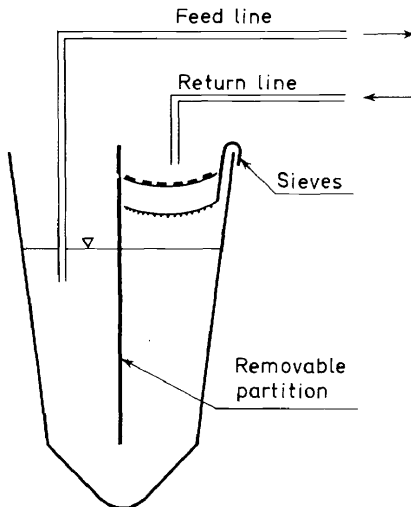


Figure 1. Proposed design of feed tank for cutting fluids.

It is fairly common that a conveniently placed group of machines is served from a common tank of cutting fluid. The stock may be one or a few cubic metres. The device makes it easy to check the general condition of the fluid, to remove scraps and deposits, and to skim off excessive oil. The important control of the oil concentration will be cheaper and therefore more attractive to carry out regularly. The hydraulic design sometimes appears to be fairly primitive, however. This may be remedied by means of a pump creating a moderate internal circulation. Such a pump will further help to keep the fluid healthy during periodical shut-downs, e.g. during weekends. Tanks of this kind and size are sometimes placed below the floor to save space. This reduces the advantages if inspections and maintenance work therefore become more uncomfortable and thus less attractive.

The installation of a separately housed central feed system offers considerable advantages. The requisite for a central system is a large manufacturing unit with homogeneous production. Such a system will easily bear the costs for automatic removal of solids by scrapers and magnetic filters, and of floating oil by skimming devices, and for quality control. A studied system of this type had a tank volume of *c.* 70 m³. The turnover time of water due to evaporation and carry-over with workpieces was 70–100 days. The corresponding turnover time of oil exceeded one year. Complete replacement of the content of the system is carried out every third or fourth year.

It is quite obvious that, although the central systems have conclusive advantages, they cannot always be used. The shop may be too small, the production too heterogeneous, or local conditions may not allow the necessary installations. If proper efforts are made to improve the design of individual feed systems, however, these will compare much better with the central systems than they do today.

Irrespective of type and design, any feed system will always be a breeding-ground for unwanted bacteria. The supplementation of the cutting fluid by a suitable bactericide is therefore indispensable if premature decay is to be avoided. It must be assumed that the user of a cutting oil will have no experience at all in this area. The bactericide manufacturers—with few exceptions—also have very little or no experience of this particular kind of application and therefore lack the essential expertise. The most sensible and safe solution seems to be that the user trusts the producer of cutting fluids to advise him on the choice and use of bactericides, and that the latter establishes cooperation with bactericide manufacturers in order to select the types most suitable for the purpose. This would guarantee to the user that any recommendation of a particular bactericide is based on the maximum expertise.

It must be stressed that bactericides used for preserving cutting fluids should be only moderately stable—as in most other applications. Additions of fresh material must consequently be made at regular intervals. The inclusion of a bactericide in the marketed concentrate has little meaning, therefore, unless it preserves the concentrate as such during storage or when the cutting fluid is used more or less in a once-through way, as may occur in very small shops.

Some observations have indicated a link between the bacterial quality of the cutting fluids in a workshop and the frequency of skin irritations. It

may also be pointed out that the necessity of discarding batches of fluids frequently because of bacterial decay indicates that the lubricating and cooling properties have undoubtedly deteriorated a good time before replacement is judged to be necessary. This has an obvious economic aspect.

It should be mentioned, too, that the performance of a cutting fluid may deteriorate for other reasons than bacterial infection. Certain operations such as grinding of hard metals cause a build-up of very fine solids which are difficult to separate. It might be wise in such cases to design a feed system which allows the stock to be run down to a low level, whereafter cleaning and complete replacement are carried out.

To summarize, the use of a make-up water of suitable quality, the improvement of the very much neglected feed systems with respect to the design of features which promote bacterial growth, and the use of adequate bactericides, will cut down the consumption of cutting fluids considerably. The costs for products, handling, maintenance and waste treatment will be affected accordingly.

TREATMENT OF SPENT CUTTING FLUIDS

It was mentioned previously that there are two basically different ways to handle spent cutting fluids. The evaporation-burning process is costly. Contractors have been reported to charge 10–20 US \$ per cubic metre (35–70 \$ per 1,000 gal.) excluding the transportation costs. Any residual nitrite has to be destroyed in advance by chemical treatment to prevent local corrosive air pollution under unfavourable conditions. The process seems to be justified only when other liquid wastes exist for which destruction by burning is the only acceptable method. A condition is then that the same furnace can be used. Another rather exceptional case is when the discharge of the water remaining after chemical treatment will cause problems because of the high BOD.

Table 1. Methods for splitting emulsions

Method	Chemicals	pH-range
Reduction of pH	HCl	1
Increasing ionic strength	NaCl, MgCl ₂ , CaCl ₂	5.5–6.1
Flocculation	Al ₂ (SO ₄) ₃ , FeCl ₃ , FeSO ₄ + CaO	5.5–8.3
Combinations of the above	—	8.0–8.4
Absorption	Various materials	—

The separation of emulsified oil and water by physico-chemical methods will in most instances give a quite satisfactory result at a moderate cost, that is around 1.40 US \$ per cubic metre (5 \$ per 1,000 gal.). Table 1 summarises the methods which may be applied and the corresponding chemicals.

It is unfortunately not possible to select an apparently suitable method from the table at random and then apply it to any spent emulsion or combination of emulsions. *Table 2* presents the results from a laboratory study of which method was best suited for treating a number of arbitrarily chosen spent cutting fluids. The chemicals indicated by plus signs in the table are those which gave the best results as judged by visual inspection of the aqueous layer for remaining turbidity. The table indicates clearly that the merits of a certain type of treatment can never be predicted but must be

Table 2. Laboratory testing of splitting emulsions

Product	$\text{Al}_2(\text{SO}_4)_3$	$\text{FeSO}_4 + \text{CaO}$	$\text{CaCl}_2 + \text{FeCl}_3(\text{FeSO}_4)$
Nynäs AK 85X	—	—	+
Houghton			
Antisep	—	+	—
Hocut 3210	+	—	—
Cindol 3201	+	—	—
Cimcool S4	—	—	+
Esso, Cutwell	+	—	—
BP, Energol SB4	+	—	—
Caltex, Cooledge	—	+	—
Castrol, Ultralin	+	—	—
Texaco			
Soluble Oil C	—	+	—
Stuart, Codol	+	—	—
Quaker Oil 43	—	+	+
Atlas Oil			
Trucut C	+	—	—
Trucut SCW	—	—	+
Trucut EP C	+	—	—

found out by practical testing. The study proved, furthermore, that any test of this type had to be carried out on used cutting fluids. Results from the testing of freshly prepared emulsions may be quite misleading and are therefore of little value for practical considerations. It was found, in addition, that the results obtained from testing a particular procedure on a particular type of cutting fluid could in fact vary somewhat according to the specific purpose for which the fluid had been used, how far it had decayed, etc.

Practical considerations suggest that all the oil-containing waste waters from a manufacturing site should be treated, if possible, by the same procedure and in the same equipment. An effort must, therefore be made to keep the number of different types of emulsions in use at a minimum. On the other hand, the personnel may claim that this or that particular product is indispensable for this or that purpose. Such claims, however, are mostly based on personal rather than on rational reasoning. It has been reported that a plant for the manufacture of gear-boxes removed some twenty different cutting fluids from stock, leaving only three emulsions, and with no apparent disadvantage. It may be desirable, furthermore, to replace certain products because they are not compatible with the treatment process which has been found to be the most suitable with respect to other factors.

It is recommended that experts should be consulted when certain wastes appear to give trouble in this respect.

Before a choice can be made between different principles of treatment, it must be decided whether a continuous or a batch process is the most suitable. This is, of course, a matter primarily of how large a volume has to be treated. Continuous equipment is available with capacities from *c.* 0.5 m³/h and upwards. Centrifuging, flotation by compressed air, electroflotation, or passage through a packed tower, is used to achieve separation. Certain procedures require the addition of energy in the form of heat.

This paper will not discuss the merits of various marketed types of equipment based on the above principles. It will instead call attention to some practical factors which have to be considered in the selection of equipment which appears to meet the need most satisfactorily.

The first step is to make a complete inventory of all existing oil-containing wastes with respect to type (cutting fluids, rolling oils, wastes from degreasing etc.), quantities, and the frequency of rejects. If certain wastes contain dispersed oil or settleable solids, it is advisable to construct separate holding tanks equipped with the corresponding removal facilities. Separate holding tanks are also required for wastes having an extreme pH.

The next step is to test the splitting of the individual waste waters in the laboratory. Experience indicates that preference should be given to the continuous processes based on salts of di- or trivalent metals (magnesium, calcium, aluminium or iron) with lime or hydrochloric acid for adjustment of the pH if required. Destabilization of emulsions by means of acidification to a pH below 1 may give good results, but makes a final neutralization necessary. This involves a complication which appears undesirable in view of the conditions prevailing in practice.

The initial testing may be done on sample volumes of *c.* 1 litre, and interpretation of the results will require considerable experience and judgment. The results are informative but will not always give direct information as to whether a full-scale process will fail or succeed. We have seen cases when magnesium chloride, for instance, occasionally gave poor results in the laboratory test but very good ones in a full-scale process, although the conditions were made as identical as was practically possible.

The shortcomings of laboratory tests are not so serious as to render them valueless. It is advisable, on the other hand, to supplement them by pilot-scale tests before the final choice of equipment for a continuous process is made. Some manufacturers have recognised the desirability of testing on a larger scale and have consequently constructed mobile pilot units. These will give the prospective customer an opportunity to test the performance of the offered equipment on his particular combination of wastes under realistic conditions. Such pilot testing is strongly recommended, especially as there are limited possibilities of modifying the operating conditions of a continuous process once the corresponding equipment has been designed, delivered and installed. Many manufacturers will be prepared to claim that their equipment will do the expected job properly. If such claims are not based on tests in the actual shop, their acceptance may often lead to considerable disappointment.

The splitting of emulsions will result in an oil fraction and in a more or

less clean aqueous phase. The oil is preferably mixed with fuel oil and burnt in a steam or power plant, or used for an unqualified purpose, while the water is conveniently treated together with domestic and other waste water in a municipal sewage treatment plant. An oily, fairly sticky sludge will be formed in addition. The quantity and properties of this sludge will depend on the character of the original wastes and on the type of chemical used for the treatment. They have to be predicted with some accuracy, as the sludge has to be dealt with separately. The mechanical and dewatering properties of the sludge are normally greatly improved if a synthetic flocculant is added at a suitable stage of the treatment. The quantity needed is too small to have any effect on the treatment costs, except those for sludge handling, which are favourably affected.

Treatment will also be a concern of the smaller workshops. Although each unit may produce a few hundred litres a day or less, the combined polluting capacity of the smaller units of an industrialized area may be of considerable significance. This is accentuated by the fact that a number of shops may dump waste almost simultaneously, either on Friday afternoons before the weekend shut-down or on Monday mornings when it is found that part of the stock has gone sour. These shops, furthermore, will undoubtedly not have personnel who are competent within the waste treatment sphere. A condition for carrying out any form of treatment in such shops is that a set of 'cookery book' instructions is available. The above remarks will apply also to some extent to medium-sized mechanical engineering shops.

It may be difficult to decide who is to be responsible for providing the desired simple instructions. A basic principle of modern environment protection is that the manufacturer of a chemical or a formulated product cannot decline the responsibility for its effect on the environment unless improperly used. This principle will assist the small and medium-sized workshops. They may require that the advice of the supplier of cutting fluids is not restricted to the function of his products in the manufacturing operations, but that it should also include very practical information as to methods for treating them once they have been turned into waste.

Obviously, however, the supplier cannot be asked to cover all situations. The many instances in which the total oil-containing wastes are made up of a complex mixture necessitate that advice is available from more widely experienced personnel. We have found that the many practical and difficult to solve problems in this field make it very desirable that supplementary resources for service and consultation should be created.

Laboratory tests are quite satisfactory for establishing the proper conditions for the discontinuous splitting of emulsions. The choice of chemicals is somewhat wider than in continuous processes, as the time factor is less critical. The separation may be left to take place overnight, for instance, once suitable chemicals have been added. A simple tank with a bottom outlet is quite adequate. An oil level indicator just above the bottom valve is helpful. Large tanks should be equipped with a device for stirring, either mechanically or by compressed air. Using an empty barrel as splitting tank and removing the separated oil by skimming may be acceptable in very small shops as at any rate better than nothing.

Some mention should be made of the use of solid oil absorbents for treating

emulsions. The material B20, marketed by Degussa of Frankfurt am Main and consisting of a hydrophobic silicate material, is one example. Certain types of bark have similar properties. Absorbents like B20 give excellent results in terms of oil removal, but are somewhat expensive. The cost corresponds in Sweden to *c.* 20 US cents per litre of absorbed oil. This means that the cost for treating one cubic metre of a 3 per cent emulsion will be around \$6 (*c.* \$20 per 1,000 gal.) exclusive of the cost of equipment and personnel. This should be compared with the \$1.40 for treatment with salts of di- or trivalent metals. The large volume of the resulting fairly sticky sludge presents a certain disadvantage. Absorbents of this kind are excellent, however, for polishing the effluents from a treatment process. Polishing is often desirable, especially when large volumes are to be treated. This is because the practical conditions, e.g. with respect to the composition and properties of the wastes, vary sufficiently to make the result, in terms of oil in the final effluent of any treatment process, subject to variations. A small tower filter or a stirred tank filled with an absorbent of this type and having an outlet in the form of a filter may then do a good job at a low cost.

Any kind of treatment will have a reduced value if the oily sludge cannot be removed satisfactorily. The use of synthetic flocculants will improve the mechanical properties, making the dewatering and subsequent handling more trouble-free. Satisfactory final destruction of the sludge will require burning, e.g. in a plant for incineration of household garbage. The use of furnaces in the pulp industry for the burning of bark has been suggested in Sweden. Open pit burning should be avoided for reasons of air pollution. Placing the sludge on a dump is completely inappropriate because of the potential risk of ground-water pollution.

The transfer of the sludge from the shop to a municipal incinerator, for example, will require a service system for collection and transport. This will ensure also that the sludge from small and medium-sized plants is removed in a workable way. It seems practical that the system should be organised on a municipal or regional basis. Local or regional initiative and participation appear accordingly to be a requisite for a fully satisfactory solution of the pollution problems emanating from oil products used in manufacturing operations.

EFFLUENT QUALITY CRITERIA

The negative effect of dispersed mineral oil on, for example, an activated sludge or anaerobic sludge digestion has been investigated.² The effluents in question, however, contain emulsified oil. No information has been found concerning the interference of oil in this physical form with the biological systems mentioned.

The efficiency of a process for the removal of oil is normally assessed by estimating the concentration of residual oil in the final effluent. The term 'oil' will then be defined by the analytical method used. The German method H17/18 uses extraction with light petroleum³. The solvent is then evaporated and the extracted oil weighed. Light petroleum will also extract materials which cannot be considered as mineral oil in the sense of a mixture of hydrocarbons. The extraction of such materials is reduced somewhat either by using pentane as solvent instead or by redissolving the evaporated extract

in light petroleum, filtering it and evaporating it to dryness again. Purification on an alumina column may also be employed. To obtain a measure of what are strictly hydrocarbons will require chromatographic purification of the sample followed by infra-red spectroscopy. The accuracy of oil analyses is highly dependent on proper sampling and proper sample storage. Data of the efficiency of different treatment processes can never be compared unless the whole procedure from sampling to final analysis is carried out in an identical, strictly standardised way. There are unfortunately no instructions in this respect concerning the H17/18 method.

The ambiguity of the analytical methods and the lack of information on the properties of small amounts of emulsified oil on biological systems render any prescribed limits for maximum allowable concentration of oil in these types of effluents fairly arbitrary.

A respirometric method devised by Offhaus⁴ offers a means of obtaining preliminary information on the properties of a treated emulsion and on its capacity to interfere, for example, with an activated sludge process. The principle is illustrated in *Figure 2*. The sample, a standard peptone solution

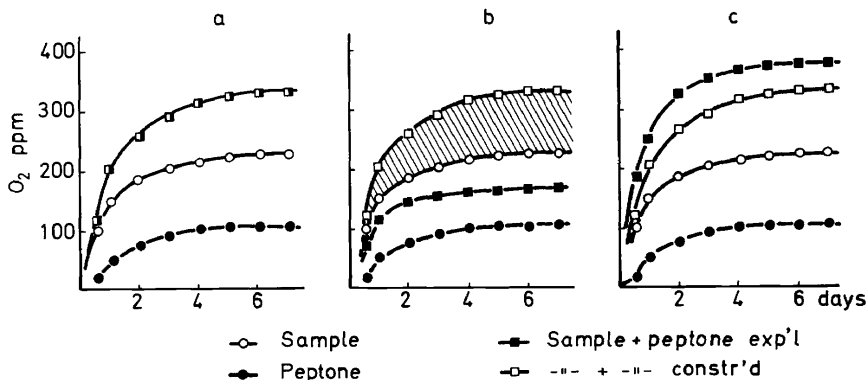


Figure 2. Principal interferences with seed activity according to Offhaus⁴.

and a mixture of the two are each supplemented by the nutrients used in the standard BOD test and then seeded with a sufficient quantity of settled domestic sewage. The consumption of oxygen is measured and plotted against time. The curve representing the sum of the individual curves for the sample and the peptone is then constructed. There are three possible cases:

(a) The constructed curve and the experimental curve for the mixture coincide. There is then no detectable interference of the sample with the activity of the seed.

(b) The constructed curve falls above the experimental curve. This is explained by a negative interference of the sample with the degradation of the peptone, i.e. a toxic or inhibitory effect is obvious. The area between the two curves gives a qualitative measure of the toxicity of the sample.

(c) The constructed curve may fall below the experimental curve. This indicates that the presence of an easily metabolized substrate, i.e. peptone,

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accelerates the degradation of the sample. This effect is most probably due to a delayed adaptation of the seed to the sample when the peptone is absent.

The instrument of choice for such studies would be the Sapromat manufactured by the German company E. Voith GmbH (*Figure 3*)⁵. It is an ad-



Figure 3. Sapromat AP 6, manufactured by E. Voith GmbH.

vanced instrument, involving a cost of about US \$40 per test. This has been considered to be too expensive for routine work. The simple equipment for measurement of BOD manufactured by Hach Chemical company (*Figure 4*)⁶ gives sufficiently accurate data for routine purposes at an equipment cost of *c.* \$3 per test. *Figure 5* compares the performance of the two instruments. The higher oxygen consumption indicated by the Sapromat is readily explained by the fact that this instrument is based on a first order reaction and the Hach instrument on one of second order. The run was discontinued on day 5 as nitrification started to be apparent in the Sapromat. Nitrification did not begin in the Hach equipment until day 9. The Hach test shows a slight inhibition which is not apparent in the test run on the Sapromat.

Figure 6 shows the data from an experiment in which the sample was treated at two different levels of added chemicals. The different oil concentrations are reflected in the oxygen consumption (BOD values). The difference in BOD corresponds to about half the theoretical value for the complete oxidation of a saturated hydrocarbon present in the amount indicated by the oil analyses. No toxic effect is indicated. *Figure 7* presents the results of samples treated to < 1 and 480 ppm of residual oil, respectively. The 400 ppm sample is oxidised somewhat more slowly. No toxic effect is observed. The oxidation is evidently accelerated by the peptone and would certainly be so

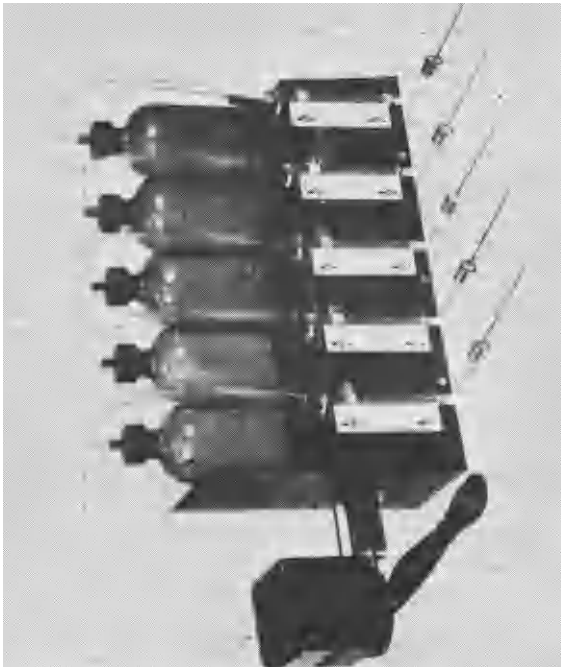
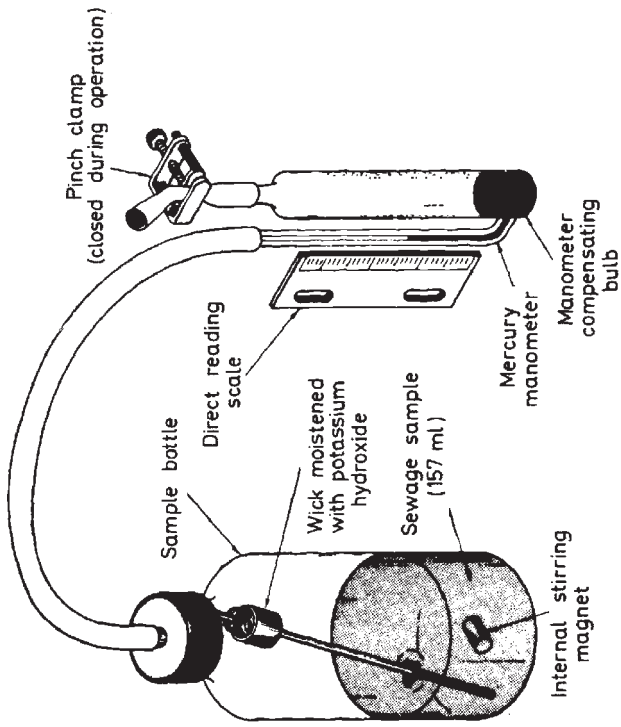


Figure 4. Hach Manometric BOD Apparatus⁶, manufactured by Hach Chemical Co.

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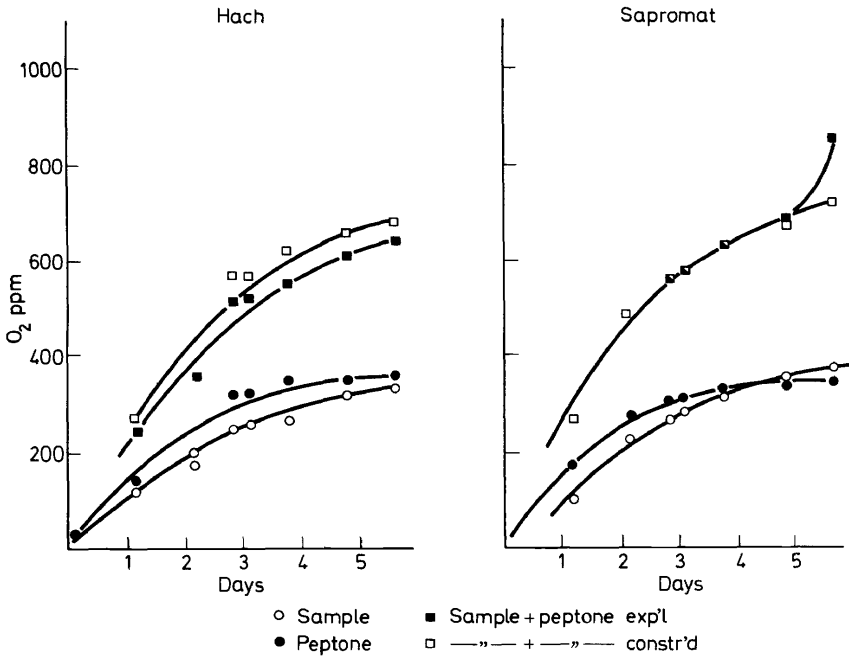


Figure 5. Comparison of performance of Sapromat AP 6 and Hach Manometric BOD Apparatus.

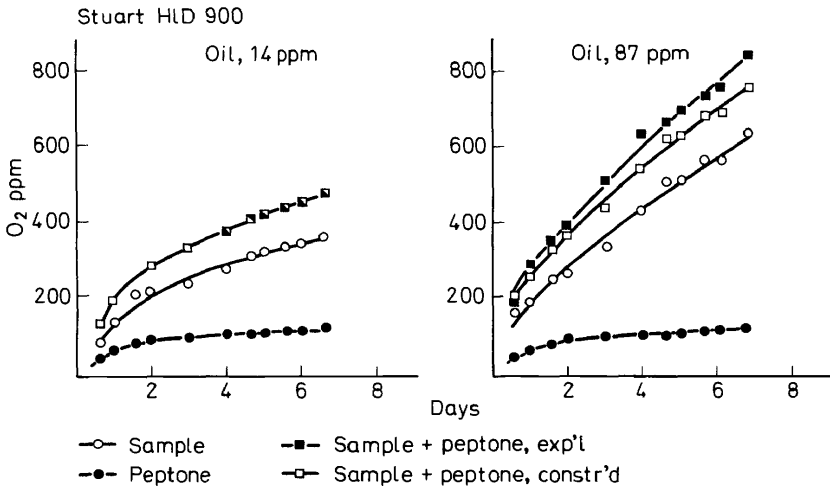


Figure 6. The influence of the amount of chemicals used in the treatment of emulsions.

Codol

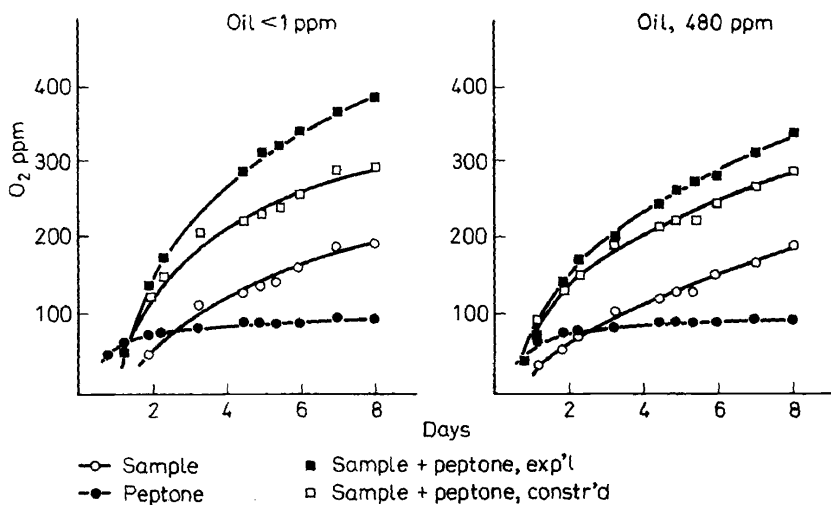


Figure 7. The influence of residual oil content on the rate of biochemical degradation.

Cindol

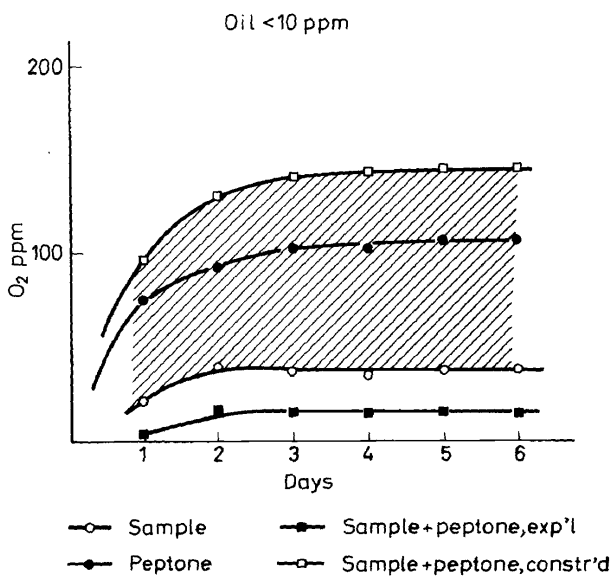


Figure 8. Case of inhibition at low residual oil content.

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in the presence of any easily metabolized substrate. The oil present in the last-mentioned experiment appears as a biologically inert material under the conditions used.

Finally, *Figure 8* shows a case of inhibition. The toxic effect does not appear to be attributable to oil but is better explained by the presence of a bactericide.

The biochemical oxidation of nitrite to nitrate has not been taken into consideration in the above studies. A refined technique may have to include a step in which the nitrite is either oxidised to nitrate or reduced to elementary nitrogen beforehand. The studies will also have to be supplemented by an examination of the effect of effluents on activated sludge and on anaerobic digestion of sewage sludge at different levels of oil. The results indicate, however, that data of oil concentration as estimated by an extraction procedure are no more than a primitive measure of the performance of a treatment process with respect to whether the treated water can be safely discharged to a sewage works or not, at least when the concentration falls below 100 ppm. They may be useful as a basis for judgement in cases when the treated water is discharged directly to a watercourse, but less so when discharged and treated together with domestic sewage. The observed effects attributable to bactericides indicate that an unwise use of such materials may cause more problems than any oil present, at least in the case of effluents from large production sites.

CONCLUSIONS

The satisfactory control of pollution caused by the use of emulsified oils in the mechanical engineering industry is not just a matter of constructing and operating a treatment plant. A number of practical problems relating to the in-plant handling and use of emulsions have to be identified and solved. Pollution control within the discussed field includes a significant element of cost-saving.

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