

of the fatty nitrogen compounds. However, the Wijs method is modified somewhat from that used for fatty acids. The definition is the same as before and is expressed in terms of centigrams of iodine absorbed per gram of sample. The method is applicable to fatty amines, diamines, amidoamines except those containing conjugated unsaturation. The IV method for amines differs in that glacial acetic acid is used as a solvent instead of carbon tetrachloride, and mercuric acetate is used as a catalyst. Wijs reagent or iodine monochloride is used as in determining the iodine value of the fatty acid. Somewhat more care must be taken than when determining the iodine value of fatty acids. The precision is not as good as with the fatty acids. It is interesting to note that some amines are sold with IV specifications that are tighter than the precision of the method is able to deliver. However, the method is very useful in helping to identify amines and characterize them for certain applications.

The unsaturation of fatty quaternary ammonium compounds is also measured using a modified Wijs method. Chloroform is used as a solvent. Sodium lauryl sulfate is also added to prevent the free iodine from being held tenaciously by the nonaqueous phase. The technical reason for this is that sodium lauryl sulfate reacts with the quaternary and prevents formation of a quaternary triiodide. Although this latter compound is quite soluble in chloroform, it releases the iodine slowly. The last wet methods I would like to discuss are those involving the determination of long chain quaternary ammonium compounds. This is one of the most interesting areas in the analytical chemistry of fatty nitrogen derivatives. There is only one official AOCS for quats involving their quantitative analysis. This is a method for the average molecular weight of fatty quaternary ammonium compounds (TV 12-64). This is rather misleading because this method using perchloric acid as a titrant combined with mercuric acetate as an anion transfer agent is really a method for halides (3). It is not applicable to sulfate quats. When all the corrections are made for nonquaternary components, the molecular weight can be calculated.

A great deal of analytical talent and effort has gone into methods for determining quaternary ammonium compounds. The best known are those that use solvent partition systems in which a long chain anionic surfactant is used to

titrate a quat in the presence of anionic dye or indicator (3-5). The anionic indicator which is normally water soluble complexes with the quat to be solubilized in a water immiscible solvent such as chloroform. The anionic titrant replaces the dye in the quaternary complex. When there is no longer any color in a water immiscible solvent, the titration is complete.

Recently the AOCS has been testing a system for titrating quaternaries that uses sodium tetraphenylboron (TPB) as a titrant (6). The titration is performed in water in the presence of dichlorofluorescein indicator. This indicator normally is yellow in aqueous solution, but in the presence of a long chain quaternary a pink complex is formed. As TPB is added to the system the quaternary precipitates. When all the quat is precipitated, the indicator suddenly changes from pink to yellow. The method can be used not only to determine the chloride quats but also the quaternary ammonium sulfate salts.

There are AOCS official methods for ash, pH, solids, nonamines, flash point, and moisture in the various nitrogen derivatives. The criteria for these determinations are self evident and won't be discussed at this time.

There exists a great deal of literature on the analytical chemistry of fatty acids (7) and their derivatives for those who would seriously pursue the subject. In this short presentation it is possible to discuss only some of the analytical highlights but not go into the subject in great depth.

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Pollution Control in the Fatty Acid Industry

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ABSTRACT

Operations of the fatty acid industry create wastewaters, emissions to the air, and solid wastes which have the potential of insulting the quality of the environment in a number of ways. Some of the controversy and the problems that are current in the national environmental effort are discussed. As to the fatty acid industry prospects, some attention may come to the industry if toxics are found to be in the industry's wastewaters. New air emissions permit will be difficult if not impossible to obtain. Long delays and expensive data gathering will be involved. Disposal of solid waste classified as hazardous materials will become extremely costly and involve much paperwork. Wastewaters can originate from any of the process steps: spills and tank bottoms from

receiving and storage, foots from alkaline extraction pretreatment, condensate from pressure reduction after fat splitting, condensing water and condensate from fatty acid distillation, and condensing water from glycerine evaporation and distillation. The organic matter in the wastes is biologically degradable so one pollutional effect is reduction of the oxygen level in receiving streams. Oil not in soluble or finely dispersed state is objectionable for the additional reason that it forms slicks or films in the water surface. Fatty acids in soluble forms are toxic to fish in fairly low concentrations. Heavy metal catalysts used for fat splitting or hydrogenation such as zinc are objectionable at trace levels. Source control methods include good operator attention to minimize avoidable losses, optimum recovery of fatty acids and

oil in recovery steps, mist eliminators and entrainment separators in distillation and evaporator vapor conduits, and use of indirect condensers in place of direct spray condensers. Treatment of wastewaters includes removal of floatable fat and fatty acids by gravity settling. The residual wastewaters so pretreated are susceptible to treatment processes using bacteria for their degradation. Most fatty acid producers discharge the wastewater to municipal systems in which they receive biological treatment along with residential sewage. Air emissions are minimal for the standard criteria of particulates, organics, etc., because of the low vapor pressure of the materials involved. Odor is not subject to federal legislation, and local regulations and circumstances of concern vary. Odors originate from storage tank vents, from noncondensables vented to the atmosphere from condensers on pressure-relief operations, and from stills. Cooling tower recirculating systems may release odors condensed in the condensing sprays, or odors may be generated from bacteria growth in the system. Odors are controlled by wet scrubbers on off gases and by conveying the gases (air) to the boiler as air supply. This practice incinerates the odor-producing compounds. Solid wastes include spent clay used in pretreatment and foots from glycerine stills. Deposit in sanitary landfills is the usual disposal. If solid wastes contain much metal catalysts, their disposal must be to special sites approved for hazardous waste materials.

The 1970s is a decade that the environmentalists proudly refer to as the environmental decade. This ten-year period brought about the passage of major federal legislation covering all environmental media: water, air and land. In 1970 came the Clean Air Act. In 1972 the Federal Amendment to the Water Pollution Control Act. In 1976 the Solid Waste Disposal Act and finally in 1978 the Resource Conservation and Recovery Act. Recently quite a voice of concern has arisen, a concern that the EPA has interpreted the laws such that their regulations may be more severe than is best for the country. Change may come about via litigation of the regulations in federal courts. About midway in the environmental decade came the beginnings of the use of the federal courts to speed up or modify environmental activity. Some industrial firms and trade associations, perhaps from witnessing the success of the environmentalists, have followed with court challenges to many significant environmental regulations issued in the last year or so. They have had several successes. In fact, organizations are vying now to launch court challenges to federal regulation, literally waiting in line at the court doors to be the first to file suit when a controversial regulation is issued. Being first will give them primacy in some respects, particularly in the choice of the federal court in which they will appear. The litigation, or the antiregulation proliferation sentiment, or matters of economics, may bring about a new look at what we can afford and may moderate the interpretation of the laws. It may lead to even altering the laws. Of course, all want laws that adequately protect health and the environment. One fundamental issue is the definition of a safe environment. What factors of assurance are used, and what consideration is given to the economics involved?

All of the air and water laws and regulations are fundamentally aimed at selecting concentrations of substances in the air we breathe, the water we drink, or the water aquatic organisms live in, which are safe. The term "safe" is used advisedly. There are degrees of safe. As safe as can be afforded? As safe as can be accomplished without giving up

the utility of some product or material? As safe as technology for removing a material from water or air? As safe as a healthy adult needs? As safe as an older person, one suffering from emphysema, asthma, high blood pressure and failing kidneys needs? As safe as a newly hatched mayfly larva needs? Or as safe as is acceptable by society? The subject of control limitations may be referred to as "risk management." This term implies that the exposure level can be managed, i.e., closely controlled. Plus it implies that a certain chance or risk of health damage would be accepted.

Science and technology is generally unable to determine precisely the absolute safe level of many substances of biological significance. Test procedures are, as a practical matter, limited to exposing some test organisms experimentally in a quite limited way. The environmental conditions of the test are limited; the number and types of species exposed are limited; the length of time of exposure is limited. Only the death or survival of another species, a surrogate for humans, is readily observed. The toxicologist has sophisticated methods or techniques projecting observed damaging concentrations to low, long time exposure, threshold-effect levels. They are hopefully able to relate the incident level with concentrations. Another standard of safety is the observation of the health of people or any life forms which have been exposed in real life for periods of time to the pollutant in question. For example, hospital admittance records for difficulty in breathing and so forth, and the levels of certain pollutants in the air of that community can be correlated to uncover some risk level. A great debate is taking place and will continue to take place as to the proper way, the proper model to use, the proper reasoning to employ, to arrive at no effect levels or levels at which a risk is tolerated. The objective of absolute safety may be untenable. On the other hand, society may wish to accept a risk less than that which cannot be effectively discriminated from background risk or of other activities which individuals do accept. Richard Wilson, at Harvard University, has tabulated some interesting occupational risks. In playing football, for example, the average risk of death in any year among all participants is 4 in 100,000. In horse racing for the jockeys it is 1.3 per thousand per year. For canoeing, for those spending at least 40 hours per year engaged in that activity, the risk is 4 per 10,000. For rock climbing, for each 40 hours per year engaged in this sport there will be one death in a thousand participants. Of course the ease, or the lack of ease, by which the risk may be reduced enters into the acceptance, as does whether the decision is one's own personal choice or a choice made for him by society.

One can hope to have the best of both worlds, a safe world and an affluent world; a world in which the products are reasonably priced. Hopefully the experts can arrive at the right answers. Someone has said that for every expert there is an equal and opposite expert. In this great debate may the best expert win. All society should be involved, all the experts, all concerned individuals, the activists, and the silent.

These thoughts on the fundamentals of what is behind environmental control by way of basic planning decisions and problems will set the stage for a few remarks on how the laws and regulations have impacted or may impact on the fatty acid industry. The impacts apply more or less to the animal and vegetable oil refining industry and the soap-making industry with which some of use are associated.

In the area of water pollution control, the water pollution laws are structured for two fundamental industry groups, classified in accordance with the practice in waste disposal. Those that discharge wastewater directly to the nearby water course, be it a lake, river, or stream comprise one group; those that discharge their process waste to public-owned treatment works comprise the other. These two groups are known in the trade as direct and indirect

dischargers, respectively. The fatty acid producers appear to be made up for the most part of indirect discharges, although there were, and perhaps still are, plants which discharge condensing water to the nearby stream and the remainder of the waste to the publicly owned sewers. The discharge of condensing waters that are at times significantly polluted with entrained or condensed organics directly to nearby water courses without treatment has been halted in some cases, I believe, and replaced with recirculating cooling water systems. The blowdown from these systems is discharged through the municipal sewers. The direct dischargers have been subject to national permit limitation programs, the NPDES program, since 1972. The federal water pollution control law also requires that limitations specific to particular industrial categories be developed, called industry category limitations. All industry categories are eventually to be covered under this program. The issuing of the direct discharge permit occurred years ahead of the developing of the industry category limitations for many of the industry categories, including the fatty acid industry. The fatty acid industry has not been the subject of any specific EPA industrial category limitations to date and likely will not be for some years in the future. In the meantime the industrial plants who are direct dischargers have been complying with discharge permit limitations developed in the absence of industrial category limitations for them. The national category limitations may not make any difference when they are issued.

The work of developing a wastewater discharge guideline for the fatty acid industry by EPA is interesting. The law names certain industry categories for which the EPA was to develop these guidelines. These constituted a first wave of regulations. One of the industries named in that first wave was the soap and detergent industry. The initial basic process of the fatty acid industry and the soap industry are practically the same so there was the possibility that the EPA could choose to include the fatty acid industry as one of the subcategories of the soap and detergent industry. A group of industry representatives, which is organized as part of the Soap and Detergent Association, and is known as the Fatty Acid Producers Council, decided in consensus that the coverage of their industry as a subcategory of the organic chemicals industry was more appropriate than being considered a part of the soap and detergent industry. This group requested such coverage from the EPA. The EPA was agreeable. Data on fatty acid processing waste was obtained by the EPA, both by soliciting available information from industry and a sampling and analytical program at selected plants. These data were compiled by EPA and returned to industry participants for comments. Some companies found the data unrepresentative and objected to it being used as a basis for limitations. There were several other subcategories of the chemical industry which had similar problems with the data base that EPA had developed. EPA decided to drop the fatty acid subcategory from inclusion in the initial industrial discharge limitations for the chemical industry. This delay is probably going to extend for several years. The reason why this delay is likely centers around a change in the last couple of years in the priorities of the EPA program. The reason the EPA has not completed the work of developing limitations for all industry categories is that they have been occupied exclusively in the last two or three years with the control of pollutants which are toxic to fish or are a significant threat to human or aquatic organism health. The guidelines and standards for the food industry and the like, the nontoxic industries, has been postponed. In the early years of developing these guidelines, the EPA concentrated on pollution parameters of a more general nature; those that measure all biodegradable organics or all suspended matter as opposed to analysis for specific identifiable compounds. The EPA has been busy since 1976 setting limits for sixty-six selected classes of toxic materials

and 129 unambiguous compounds making up these classes. A list of 21 industry categories has been selected for development of guidelines for best available treatment for these toxics and for limitations in effluents. The chemical industry is one of those categories, but the EPA is concentrating on those subcategories of the chemical industry which are more likely to have or are known to have one or more of the 129 toxic compounds. As far as I know, the fatty acid subcategory is not one of the subcategories for which regulations are scheduled to be developed very soon. Incidentally, the soap and detergent industry has received attention to determine if their waste has significant quantities of these 129 compounds. The EPA has made a preliminary finding that the 129 toxic compounds of interest are not present in the main soap and detergent SIC category. The industry will petition EPA for exemption of the industry subcategory from the development of guidelines for these 129 compounds.

Whether or not the fatty acid industry is ever included in this program of toxic substance limitations will depend on the EPA finding, or being advised of, toxic substances present in the industry's waste. Certain heavy metals, such as copper, are on the toxic substance list. If these materials are present in the waste, limitations are likely eventually to be set under the industry limitations program. Materials may be added to this list of toxics at any time and most materials found to be toxic will be added sometime over the next few years.

One processor of edible oils has reported a rather high concentration in oil wastewaters of one of the toxics which is on the EPA list, and this toxic is referred to as phenol. The phenol content of most interest to water quality in this group of compounds is that composed of the single aromatic ring having one hydroxyl group attached directly. Unfortunately, it appears that the analytical method for phenols used in wastewater industry includes tocopherol, from soybean, and gossypol, from cotton seed. Phenol has been reported in coconut oil distillate waste. Unless more specific analytical procedures are used, or unless these phenol compounds in the oil processing waste are shown to be innocuous, there could develop a limitations-setting-effort for such oil processors. Turning from the direct dischargers to the other group of industries, the indirect dischargers, this group can expect that EPA will eventually set limitations on any toxic pollutants that the fatty acid industry is found to have. These toxics will be controlled by limitations in discharges to publicly owned treatment works. Such limits can be adjusted in accordance with the effectiveness of the publicly owned treatment works in removal of pollutants. For phenols and any other toxics this adjustment will be important. If dischargers have the metals used as catalysts in their waste, or if phenols are given attention, this group of industry will eventually be regulated.

With regard to another indirect discharge matter that has plagued the industry, namely, limitations on oil in discharges to municipal systems, I am pleased to report that the EPA appears to maintain that animal fat or vegetable oil in dispersed form is treatable in municipal systems. They officially proposed last August that oil be declared a conventional pollutant and have indicated as of May, 1979, after they received comments on this proposal, that they will maintain this position. Classifying oil as a conventional pollutant is practically equivalent to saying it is treatable by municipal wastewater treatment process; therefore, the industry can proceed with some support or at least no interference, on the part of the Federal EPA, in convincing municipal authorities where our plants are located that there need be no limit on routine concentrations of dispersed oil in our wastewater. I must supplement this piece of good news with some additional potentially bad news in the water pollution control area, and this bad news involves

a piece of Federal law involving spills of oil and hazardous substances. The law makes the responsible party liable for the cost of removal, clean-up, and mitigation of the spill. This can amount to millions of dollars, and there is a problem with obtaining insurance against this possibility. So Congress and the EPA are favoring the creation of a super fund to cover clean-up costs. There would still be penalties for spills, but the clean-up cost would be covered at least partially from this super fund. The catch is that this super fund is to be created from a fee on each barrel of oil refined or processed, or each chemical processed per unit quantity. If this plan is carried out, fatty acid industry people and edible oil refineries may be included in this super fund charge system.

Now for a brief look at air emission control. Air emission control for boilers is a fact across the land and extends to all industry categories. The Clean Air Act Amendment of 1977 is currently coming into play, and all areas of the country have been classified as to whether or not they are in compliance with ambient air quality standards for five air quality parameters that are now in use. The nonattainment areas face severe restrictions on new sources or new emissions. In fact, an offset policy prevails which makes it necessary to reduce existing emission as much or greater than any new emission load. In the areas where the national ambient air standards are being met, a policy of nondegradation exists which makes it also difficult to obtain permits for new sources. The states must submit a plan to meet the ambient standards if they are not in compliance. They must have submitted a plan by January, 1979. They must in time meet these standards. Many areas face further reduction orders, and even restrictions on automobile traffic and use, to do this. The automobile engine size reduction and combustion control measures do not appear to be very promising in achieving much of this improvement, even though they constitute about 60% of the load in typical localities. Many of the regulations mentioned are under litigation by the trade association and probably will be delayed a year or more before they are put into effect, and probably will be modified.

The chemical industry is being studied and surveyed for air emissions, and new source performance standards are to be set for particular products. As far as is known, the fatty acid industry has not been scheduled to be addressed in this program. Emissions of the fatty acid subcategory have not been considered significant enough to warrant placing on the schedule. In other words, other sources are considered more important. The air emission information and standards work actually has three approaches, any one of which could eventually impact on the fatty acid industry. Information is issued on certain materials, for example, vinyl chloride; and on special industrial categories, for example, byproduct coking; and certain generic operations, for example, distillation. One of these may eventually come along which will apply to the fatty acid industry, but nothing applicable to the industry is expected before the early 1980s. This is balanced by the fact that the states and

the local people are implementing the ambient air quality plans, the state implementation plans, so that regardless of whether there is a category guideline or not, controls are going to be imposed.

The Clean Air Act also contains another provision of great interest to the fatty acid industry and that is it directs the EPA to make a study of odor problems. Currently odor problems are merely addressed as a local situation. They are to report to Congress on the need for a national odor control program. The EPA has contracted for this study with the National Academy of Science. A task group in that organization has been working on this project. The date of their report and the actions of Congress is probably several years away. Chances are with the charge of over-regulation that there will not be any federal involvement for some years.

Under the Resource Recovery and Conservation Act, the EPA is defining hazardous waste (solid wastes) and controlling disposal of these so that groundwater is adequately protected. Land application is controlled so that crops in the human food chain are not exposed to harmful amounts of toxics and so that the air in the vicinity of the disposal site also poses no threat to health. The EPA is also controlling sanitary landfills that are used for common household garbage and refuse so that environmental considerations are properly taken into account in the operation of these facilities. The first proposed EPA definition of hazardous waste includes the heavy metals which are on the primary drinking water standards list. Zinc, copper and chromium are three of them. So, spent catalysts of this variety from the fatty acid industry are going to be classified as hazardous waste when these regulations become final a year or so from now.

The significance of this is that the disposal must then be to a hazardous waste approved facility. For such approval a landfill must have extremely reliable protection to prevent the contamination of groundwater. A great deal of paperwork will be involved and the cost will be many multiples of the cost of disposal to a landfill of the type approved for household refuse. A further factor here is that controls on sanitary landfills for household garbage and refuse will likely prohibit the disposal of liquid slurries in landfills receiving household garbage and refuse. The reason is to reduce the volume of leachate, which is the liquid drainage from a landfill. A reduced volume of water will reduce the possibilities of groundwater contamination. The practice of putting a slurry into a sanitary landfill used for household garbage and refuse will probably be cut off.

In addition to naming specific substances in solid wastes, EPA has proposed test procedures to determine if the waste material is hazardous. The procedures consist of extracting the solid waste with an acid solution and testing it for toxicity, for mutagenic effects, and so forth. So, down the road it looks like the disposal of spent catalyst will be expensive, and waste materials with toxics which are uncovered in tests, if any, may also be a problem.