ENVIRONMENTAL ASPECTS OF SILVER HALIDE PROCESSING

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Abstract: This paper will provide a review on aspects of waste streams resulting from the processing of black and white silver halide based photographic materials. Some of the aspects that will be covered include:

1. A brief overview of regulatory aspects and their jurisdictions (federal, state, local) and silver halide graphic arts films expected directions for regulations.
2. Component characterization, contributions and disposition of materials in silver halide based processing waste streams.
3. Environmental impact of silver halide processing wastes.
4. Some aspects of practices for waste management.

Introduction

Environmental concerns are having significant impact on the operations of businesses that run chemical processes. It is therefore important to have an understanding of the regulations, the chemical processes being operated, the environmental impact of these processes and some waste control strategies. In the printing industry there are several chemical processes that are used: Printing, plate making, proofing and the silver halide graphic arts films. It is the intent of this presentation to provide a brief overview of some of these aspects with respect to silver halide graphic arts films. To a large degree, this presentation is based on information available in the ANSI Standard PH4.37 on Photographic Effluents.[1]

Regulatory Area

Regulatory aspects fall into two categories: Federal and Local.

The federal laws are defined such that the states are required to implement them and the POTW to enforce them. Federal regulations control those effluents which enter into rivers, coastal and other natural waterways. For the most part this does not directly apply to the vast majority of operations as they send their wastes to local waste treatment facilities. For these facilities, it is the local regulations that basically affect the operations of the business. However, it must be borne in mind that the local waste facilities normally release their treated wastes to natural waterways and they are therefore bound to meet the federal regulations.

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In the early seventies, when the initial environmental concerns were aired and the federal regulation process initiated, each industry was analyzed with respect to their wastes and proposed rules [2] were established for the parameters to be monitored. For the photographic industry, which was typified by the photofinishing industry, the parameters established for monitoring were total silver, cyanide, pH, total solids and BOD/COD. Cyanide was included as that was a component of the photofinishing industry at the time. It is not an issue for the Graphic Arts film industry. The initial parameters to be monitored have been revised and now are silver, BOD/COD, pH, phenols, iron, ammonia, sulfides and sulfates.

The Oxygen Demand Parameters are defined as follows:

BOD (Biochemical Oxygen Demand). The amount of oxygen consumed by microorganisms under specified aerobic conditions.

BOD_5. The amount of oxygen consumed by microorganisms in five days under specific aerobic conditions. (It is usually expressed in milligrams per liter (mg/L) or a mass per day.) Normally, BOD results are in fact BOD_5 results.

COD (Chemical Oxygen Demand). A measure of the components of a sample oxidizable by hot acidified dichromate.

It is also important to note that a waste characteristic is defined by a prescribed [EPA] test procedure. The fact that a test procedure may give improper results due to interferences by the presence of other materials, or that it is inappropriate for a specific waste does not have an effect. The test defines the parameter.

Local regulations are based in principle on the capability and/or capacity of treatment by the local waste treatment plant. Their regulations usually monitor heavy metals which includes silver, as well as phosphate and ammonium ion, pH, COD/BOD, corrosivity, flammability, toxic organics and more recently pesticides. Others may be included if of local concern. Whereas, the federal regulations did not monitor phosphate and ammonium for AgX wastes (into natural waterways) as they did not contribute significantly to this, local waste treatment plants are certainly monitored for this as they have significant quantities of this from other sources. As a result the local waste treatment facility monitor these on their incoming waters for all their sources, and so for some areas this becomes a concern especially in view of the use of ammonium based fix during the last decade. Local regulations also reflect other local concerns. For agricultural based states, e.g California and others, where the effluents go into natural water ways which are in turn used for agricultural purposes, there can be regulations on boron or other parameters that are deemed critical in that regard. Local regulations present the problem that there are a myriad of them with different concerns that do not allow simple categorizations other than they are all becoming tighter.

There are few generalizations that can be made about the local quagmires, but looking to the future we can venture some generalizations that can be made. First of all, regulation of waste will not decrease but in fact become more pervasive. Trends include requirements for discharge profiles and permits, the separation of industrial wastes from sanitary wastes leading to no discharges of industrial wastes and reduction of toxic chemical usage through permit programs. It can be noted that while the EPA has focussed on air emission concerns which do not present any problems in the photographic film areas, they have left the water waste emissions to be basically regulated at the state level. In addition, due to the latest RCRA laws there is now an additional focus on toxic aspects and in particular pesticide materials. Though the materials used in photoprocessing do not contain any of the materials on the toxics list, many waste water facilities may initially screen waste streams to assure that the toxic materials are not present.

Although waste regulation is a burden on business, it becomes justified by raising the question of the alternative being a question of the survival of society. On this basis it will become incumbent on the suppliers to provide systems that either minimize or avoid the waste concerns or provide systems that treat them so they do not provide a burden on the environment, and it will be incumbent on the operating facilities to operate their processes as efficiently as possible to minimize the environmental impact. This means that their needs to be a minimal level of understanding by the user of the chemical aspects of the processes they are running and their impact on the environment.

Chemistry of the Process

At this time I would like to focus on the chemical aspects of the silver halide process and discuss its impact on the environment.

The two basic chemical reactions that represent the photographic development process are:

Development:

The development of silver halide film is the chemical reaction of the exposed silver halide grains with a developers such as hydroquinone to form the black silver image and initially quinone, the oxidized product of hydroquinone which then proceeds to react with other chemicals in the developer. The developer contains a significant amount of sulfite ion (in the form of sodium or potassium sulfite, which serves to protect the hydroquinone from aerial oxidation. The solution is buffered at an elevated pH, about 11, which is needed to support the activity of the developer.

Silver Halide [film] + Developer ———> Silver Image [film] + Oxidized Developer

$$AgCl + \text{Hydroquinone} \longrightarrow Ag^0 + \text{Quinone Derivatives}$$

$$2SO_3^{-2} + O2 \longrightarrow 2SO_4^{2-}$$

Fixing:

The second step is the fixing of the film which is the removal of the unused silver halide by solubilizing it using thiosulfate to form a complex with the silver ion.

Silver Halide [film] + Fix ———> Solubilized Complexed Silver Ions + Halide Ions

$$AgCl + 2S_2O_3^{2-} \longrightarrow Ag(S_2O_3)_2^{3-} + Cl^-$$

From the point of view of the monitored parameters, these processes have the following impact:

Silver thiosulphate complex	Silver as a heavy metal
Ammonium thiosulfate based fix	Ammonium ion
Organics, sulfite, thiosulfate	COD/BOD
Alkaline developer, acid fix	pH
Developer & Fix	Total solids

Environmental Impact:

Silver

The first species of issue is of course Silver. Silver is considered a heavy metal and the concern for heavy metals in general is their toxicity. The issue of toxicity of silver is complicated by the fact that studies show that it is dependent on the species or form of the silver . Studies by BIONOMICS [3] and TERHAAR [4] on the toxicity of silver to bacteria and aquatic species conclude that the most toxic species of silver, by four orders of magnitude, is the free silver ion as found in silver nitrate solutions. However, the free silver ion is never found in photographic wastes. The soluble species of silver that is present in photographic wastes is the silver thiosulphate complex and this persists for only limited times. PATHWAYS [5] reported that dissolved silver, i.e. thiosulfate complex, present at a plant source, progressively decreases such that at the waste treatment receiving site, the silver is essentially all in particulate form, i.e. silver sulfide. Furthermore, once silver is precipitated, it has no tendency to redissolve.

DAGON[6] investigated the impact of silver species on waste treatment facilities and reported that the silver in the effluent from the publicly owned treatment works in the study was less than 0.01 mg/L (i.e. <0.01 PPM or <10 PPB). Waste water treatment plants removed more than 95% of the silver. An analyses by Dagon of the suspended matter in the aeration tank of an experimental treatment plant receiving only photographic processing effluents showed that there was no deleterious effect by silver (in the sludge at > 150 mg/l of sludge) on the operation of the plant which maintained an 80-95% BOD reduction.

Some other comments that can be made with respect to silver:

Silver ion is not toxic to humans. The World Health Organization has no drinking water limit for silver and silver will probably be removed from United States limits.

None of the considerations discussed have been reflected in environmental regulations.

It has been noted that the measurement of a parameter is based on a test method. Current tests use AA after a digestion procedure which measures total silver that includes any free silver ion, complexed silver as well as silver particulates in the sludge. At this time there is no accepted test method for the determination of free silver ion and since the toxic species of silver is the free silver ion, a test method that characterizes the free silver ion becomes a critical issue. An analytical method based on anodic stripping voltametry (ASV) [7] is being developed with sponsorship by the NAPM, which can selectively determine free silver ion, Ag^+, at concentrations down to 0.05 parts per billion.

BOD/COD

Dissolved Oxygen in water is necessary for the water body to support its aquatic life. Most wastes, including photographic wastes, contain materials which react with oxygen and the disposal of a high oxygen demand waste into a natural water way could be detrimental to the biological capacity of that water body. A fundamental purpose of a waste treatment plant is to provide a residence to reduce the oxygen demand. The waste treatment facility, therefore, has the concerns that its capacity is adequate with respect to what it receives, and that its incoming waste does not contain materials that are detrimental to its operation of reducing the OD by killing the bacteria either with toxic materials or overload, and also that its outflow meets the conformance requirements placed on the treatment plant.

The bacteria in a waste treatment plant are aerobic (air breathing) and it is extremely important to ensure that the treatment plant maintains a significant amount of dissolved oxygen to allow the bacteria to perform its operation in an efficient manner. Low levels of dissolved oxygen will inhibit the sewage treatment plant operation, permitting undigested sewage to be passed contaminating the receiving waters.

Oxygen demand is critical in photographic wastes because of the presence of chemicals in the processing solution which have relatively high biochemical oxygen demands and are necessary constituents for the operation of the photographic process. The primary cause of the oxygen demand from most photographic processes is due to a rather small number of chemicals, in particular sulfite, thiosulfate and developing agents, e.g. hydroquinone. Photographic wastes have a high oxygen and the only issue that they present for a waste treatment plant is that of capacity. As previously noted, it was shown by Dagon that these wastes do not interfere with the operation of the treatment plant. It is also worth noting that though photographic wastes are high in oxygen demand they are not exorbitantly so, but in the range of that of domestic wastes.

pH

The pH of photographic wastes can run from near neutral, i.e. 7, to somewhat alkaline, i.e. above 9. The pH of the developer is alkaline, around pH of 11, that of the fix is acid, about pH 4. When mixed in full use proportion and diluted with wash water, the pH is expected to be in the range of 8 to 9. However, where silver recovery systems are in place and fix is recycled, the ratio of fix to developer falls and the pH of the effluent can increase to above 9. Most sewer codes are in the range of 6 to 9 and under these conditions the waste stream can be out of compliance.

Waste Management

New less environmentally lower impacting systems are basically dependent on the supplier manufacturers. However, operation of the current processes to their best advantage with lower environmental impact is something users can practice.

Silver

Silver waste can be fairly well controlled and provides the added benefit of the value for the recovered silver. Best treatment practices would include electrolytic recovery of silver from the fix and reuse of the fix. Fix use can be cut to about 20% of traditionally recommended usage, the limiting factor being the halide buildup. Some treatment systems involving halide ion removal by ion exchange resins allow even more extensive reuse. However, as one proceeds down this path there becomes a need for analytical facilities to monitor and adjust highly reused fix. Electrolytic removal of silver from waste fix will reduce the silver to 100 to 250 ppm. Dilution with the wash waters may or may not bring the silver level into conformance with local regulations. The silver level may be reduced further to the low ppm levels required by regulations by tailing operations using steel wool buckets or ion exchange resins.

COD/BOD

Photographic wastes are readily oxidized by either aeration or biochemical oxidation and normally do not interfere with waste treatment facilities. Areas of concern for waste treatment facilities are:

(1) The actual susceptibility of the waste stream to oxidation
(1) The presence of toxic ingredients
(3) The presence of nonoxidizable substances which pass through the treatment facility and pollute the receiving stream
(4) The presence of wastes which could be converted to toxic compounds either to humans or aquatic life.
(5) Overload operations where a tank of material is discharged rapidly.
The operation of the facility may be adversely affected either by direct toxicity or by oxygen demand overload, thus reducing the efficiency of the plant. Large processors are advised to have a holding tank for such surges of waste, and discharge the waste at a uniform rate.

Waste treatment facilities may impose charges for sewer use either by volume and/or waste load as measured by BOD/COD or impose limitations on outflow. In such event, in - house treatments will be required. Such treatments can include:

Chemical methods of reducing the oxygen demand, including chlorination and ozonation.
Aeration by the installation of an activated sludge biological treatment plant or an aerated lagoon.
Hauling the objectionable wastes to where they may be discharged or treated safely.
Absorption: Reverse osmosis - concentration and hauling

Water Conservation

Water conservation is another area of concern. It is ironic that water conservation practices result in more concentrated wastes though there is no increase in the total waste load of chemicals. The benefits of water conservation are the obvious resource conservation, lower water rates and reduced hydraulic burden on a waste treatment plant. The consequence, however, is the resultant concentrated wastes and possible surcharges for high COD/BOD. Sewer codes commonly regulate pollutants in concentration units (milligrams per liter or parts per million) rather than on the basis of quantity per unit of product (pounds per 1000 square feet, etc.) as preferred by the EPA. The result is to discourage wastewater conservation because a reduction in water consumption leads to more concentrated wastes with higher BOD/COD, etc. though the total amount of materials discharged has not changed except for the water.

The greatest use of water during photographic processing is in the wash step. Most processors contain automatic water controls which turn the wash water on only when film is going through the machine. Other useful practices include the use of closed-cycle temperature regulating systems, maximum flow regulators, and the use of squeegees. Regeneration and reuse of processing solutions reduce water consumption, chemical usage, and discharges.

References

[1] PH4.37 American National Standard for Photography (Processing) - Effluents - Identification and Analytical Methods

[2] EPA PROPOSED RULES for water quality and pollution source monitoring, Federal Register, vol 39, no. 168, part III, August 28, 1974, pp 31503 - 31504. and Federal Register, vol. 51, no 125, part IV, June 30, 1986 pp 23692 - 23707. "Environmental Protection Agency, 40CFR part 136, Guideline Establishing Test procedures for the Analysis of Pollutants under the Clean Water Act; Technical Amendments and Notice of Availability of Information."

[3] EG & G BIONOMICS, The influence of speciation on the toxicity of silver to the fathead minnow (Pimephales promelas). 1983.

[4] TERHAAR, C.J.; Ewell, W.S.; Dziuba, S.P.; and Fassett, D.W. Toxicity of photographic processing chemical to fish. Photographic Science and Engineering, vol 16, no. 5, Sept - Oct 1972, pp 370 - 377.

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[7] Wang, J., Li, R and Huiliang, H., "Improved Anodic Stripping Voltametric Measurements of Silver by Codeposition with Mercury", Electroanalysis, 1989, 1, 417 - 421.