US Ink® A Division of Sun Chemical Corporation

Water Quality for Fountain Solutions

Volume II

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As litho printers become increasingly sophisticated, they realize that the key to improved quality and productivity is to understand the ink/fountain solution interaction, measure the relevant physical parameters and control them.

This report will discuss the role of the constituents of typical city water in their effect on the lithographic process, examine the case for water treatment and the various water treatment alternatives.

A. Typical city water salts level are as follows:

	mg/liter or ppm
Aluminum	1
Chloride	0-200
Chromium	0.05 max
Copper	<0.5
Fluoride	0.5-1.0
Iron	<1
Phosphorous	0-3
Sulfates	0-100
Hardness (Calcium and Magnesium)	10-300
Silicates	50-100
Total Dissolved Solids	50-500

B. Typical salts used in fountain solution formulation:

Salts	Role in Lithography
Magnesium	Scratch curing
Chromium	Anchors gum to plate
Phosphates & Citrates	Helps prevent restart scumming
Sulfates	Anti Scumming
Aluminum	Helps in proper phase equilibria

Chloride	Constituent of biocides
Silicates	Anti-tinting

It is apparent by comparing Tables A and B that several salts used in typical fountain solution formulations are naturally occurring in untreated water. This should be taken into account when reformulating etches for water treated by one of the processes described in Section D. It is imperative that a printer who installs a water treatment system of any sort, inform his fountain solution and ink supplier so that printing performance does not suffer.

C. Reasons for Water Treatment:

1. High Hardness Level:

Hardness levels exceeding 200 ppm of calcium generally lead to formation of calcium soaps in conjunction with the resins used in ink, or salts like calcium citrate and calcium phosphates, by combining with the acids found in acidic type fountain solutions.

Calcium soaps, because of their oil loving nature, lead to deposits of ink in unwanted areas such as water form rollers, molleton covered rollers, etc.

Calcium salts, because of their water loving nature, prevent ink transfer and lead to stripping on ink rollers.

Therefore, if a printing plant experiences the above mentioned problems, especially if present in all colors, water treatment is highly recommended.

2. Fluctuations in Conductivity of Incoming Water:

The dynamic surface tension of fountain solution depends on the concentration of the etch used. The higher the concentration, the lower the surface tension.

Some commercial automated feed units control the concentration of the etch to a preset conductivity. Large fluctuations in incoming water conductivity would lead to variations in etch concentration, which leads to changes in dynamic surface tension. This would result in changes in ink/fountain solution ratio, creating lithographic problems.

If the feed rate of the etch is accurately volumetrically controlled as it is in other units, this is not as serious a problem. However, severe fluctuation of water supply conductivity can still cause variations in fountain solution ink interactions and treatment may be indicated.

3. Multi- plant Customers:

Customers having plants in several cities, who wish to standardize their ink and fountain solution, generally prefer to have zero conductivity for incoming water and the etch reformulated accordingly.

D. Water Treatment Process:

There are many water treatment processes available, such as distillation, softening, activated carbon, micro-filtration, ultra-filtration, de-ionization, reverse osmosis, etc.

1. Fundamentals of Water Softening:

Water is a very complex fluid. It contains a little bit of practically everything it contacts; the air while falling as rain, the earth as if percolates into the ground, the piping as it is transported and all kinds of organic and inorganic matter it may contact in its series of uses. Dissolved minerals in water that contain an electric charge are called ions. These ions can be either positively or negatively charged. The positive ions are called cations and the negative ions are called anions. It is these positive cations, in the form of calcium, magnesium, iron and manganese that causes the hardness that is associated with water. Substitution of these hardness ions via cation exchange is the process used for softening water.

The ion exchange process requires a resin tank and a brine. The brine is sent into a tank and washes over the resin in the tank. Since the resin has a salt splitting capability and a cation accepting characteristic, sodium ions of the sodium chloride (brine) solution are attracted to the resin beads. This is called the regeneration process and it will continue until most of the exchange sites have been occupied with sodium ions.

As the complex raw water enters the tank the positive hardness ions exchange on the resin and displace the sodium ions to the service stream. Because calcium and magnesium are positive cations, they repel other positive cations. The resin, being charged with positive sodium ions, will exchange with the calcium and magnesium ions. Calcium and magnesium will now occupy the exchange sites on the resin beads. This process will continue for a length of time until the hardness ions begin to leak out the bottom of the resin bed. For all practical purpose, the resin is exhausted with calcium and magnesium and has no more sodium available to displace. This is the point where the softener must be regenerated. This softening is an exchange process and does not lower the conductivity of the water.

2. Deionization Process

Deionization is the process of removing the dissolved ionized solids from water by ion exchange. The major portion of total dissolved solids is mineral salts, such as calcium bicarbonate, magnesium sulfate, and sodium chloride. Mineral salts consist of cations and anions. Since deionization requires the removal of all ions, both negatively charged anions and the positively charged cations, materials capable of attracting both are required. These materials are known as cation exchange resins and anion exchange resins. Deionizers are fixed bed systems in which the ion exchange resins are contained in pressure tanks, and the water to be deionized is forced through the resins. The cation and anion exchange resins have a specific capacity to remove a known amount of ionizable solids. After a service run, the resins become exhausted, and are unable to remove additional ions. When the resins are exhausted, they must be regenerated with a strong acid and a strong base to restore their ion exchange capacity. A cationic resin is typically regenerated with hydrochloric or sulfuric acid. Anion resin is normally regenerated with sodium hydroxide, although potassium hydroxide can be used under certain circumstances.

Two-bed model deionizers have two separate resin containing vessels, the first being cationic unit followed by an anionic unit. Cationic resin in the hydrogen form (as it will be after regeneration with a strong acid) collects all of the positively charged cations such as calcium, magnesium, sodium and potassium, and exchanges them for hydrogen. The discharge from the cation tank is very low pH because the hydrogen combines with the negatively charged anion in the water to form acids, such as hydrochloric, sulfuric and nitric. There will be a small amount of sodium, which will not be exchanged, and the sodium "leakage" will determine the final water quality.

Two types of two-bed units are available. Strong base anion resin units remove all anions including silica and carbon dioxide. They typically produce a deionized water with a pH greater than 7, and the amount of silica remaining is usually less than 0.2 ppm.

Weak base anion units are used when removal of silica and carbon dioxide are not required. Weak base anion resin has a higher capacity at lower regeneration consumption. Since they do not remove carbon dioxide, they typically produce deionized water with a pH lower than 7.

Mixed bed units contain intimately mixed cation and anion resin in a predetermined ratio that produces extremely high quality water. Silica removal and carbon dioxide removal are usually accomplished by the use of strong base resins. Mixed bed unit pH is typically 7.0 before the water is exposed to the atmosphere, because of the almost complete deionization that occurs.

The quality or degree of deionization is generally expressed in terms of specific resistance (ohms) or specific conductance (mhos). Ionized material in water will conduct electricity. The more ions, the more conductivity and the less resistance. When ions are removed, conductivity decreases, and therefore, the water quality is purer.

3. Reverse Osmosis Process:

Reverse osmosis, as a form of water treatment, is a newer technology. The first membrane was developed in 1958. In the years following, membrane technology has grown a great deal and will continue to grow in the future. In fact, some of the membranes that are currently in use may be obsolete in the future, in favor of some new membrane material that is more resistant to a particular fouling contaminant.

The reverse osmosis membrane is used for various applications from precious metal reclamation, to chemical reclamation, to food processing, nuclear waste reclamation, laboratory water purification, etc.. We will limit our discussion to water purification and its applications.

To fully understand the technology of reverse osmosis, one must first understand the concept of normal osmosis. Simply put, in normal osmosis, water flows from a less concentrated solution through a semi-permeable membrane, to a more concentrated solution (see Figure 1). Reverse osmosis utilizes pressure to reverse normal osmotic flow, thus in reverse osmosis, water flows from a more concentrated solution across a semi-permeable membrane to a less concentrated solution (see Figure 2).

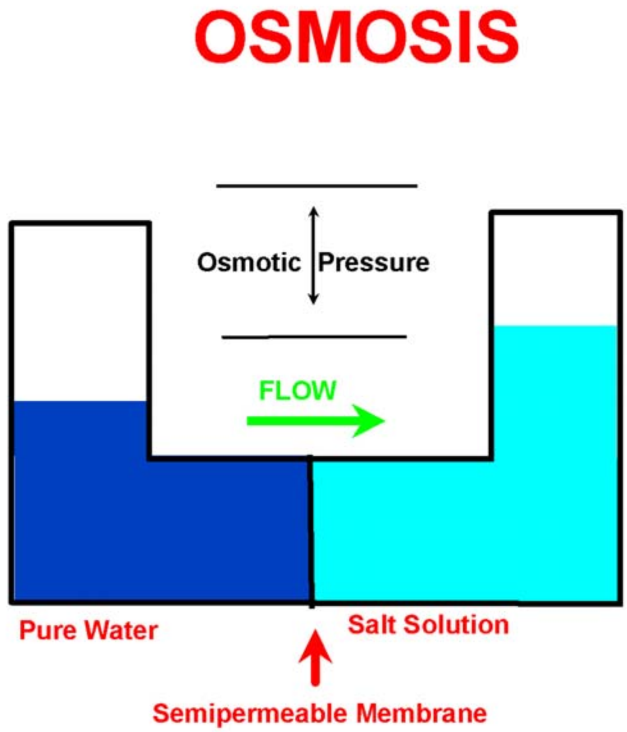

Figure 1

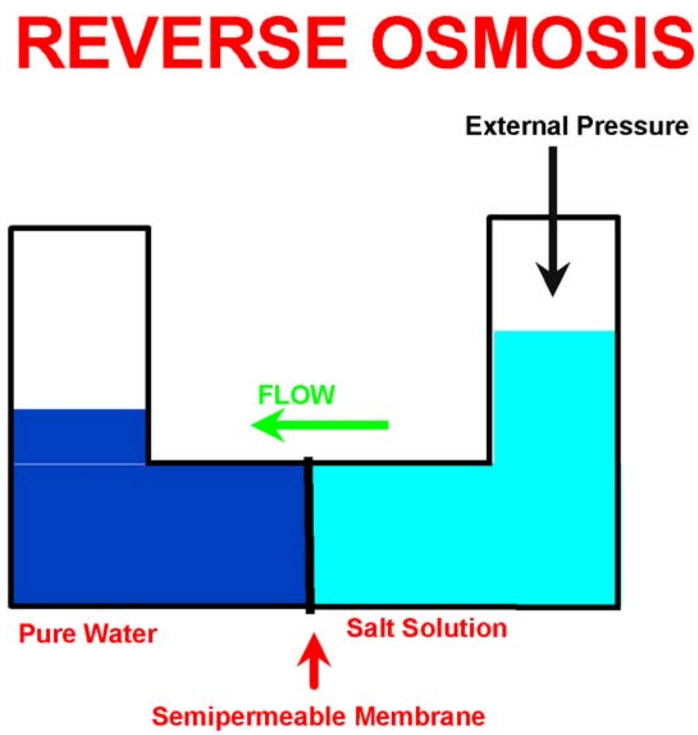

Figure 2

The mechanism employed by the membrane to remove particular contaminants relies on a combination of reactions. There is a thin porous layer on the surface of the membrane which contains a multitude of micro pores. Due to the physio-chemical interaction between the solution and the membrane, salts are rejected and only water passes through the membrane. Organics are removed dependent on their size. In most cases, this is dependent on the molecular weight of the organic molecule.

The feed water to the reverse osmosis system flows over the surface of the membrane. The pressure forces a percentage of the water through the membrane, while the remaining water, heavy in contaminants, is flushed to reject.

The movement of the water through the membrane is constantly cleaning the surface of the membrane, preventing the build-up of contaminants that could potentially damage the membrane.

Reverse osmosis is a percent removal technology. A typical reverse osmosis system rejects 90-95% of the impurities found in most potable water supplies. Because it only removes a percentage of the contaminants in a given water supply, it is impractical to predict the purity of water by this technology. Due to the mode of purification, certain contaminants are removed more effectively than others are. Polyvalent ions have better removal capabilities than others do. Polyvalent ions have better removal capabilities than monovalent ions. Large molecular weight organics (greater than 200) are effectively removed where smaller organics pass through the membrane. Gases readily pass through the reverse osmosis system and can affect the purity of the product water. Because of the relatively large size of bacteria and pyrogens, reverse osmosis effectively removes this class of impurities. Due to the removal capabilities of reverse osmosis, one of its uses in water treatment is the pretreatment of water being fed to a deionizer.

Depending on the membrane material, certain factors will affect quality and quantity of reverse osmosis water. Currently, there are three different membrane materials that comprise the vast majority of membranes used for water purification. Cellulose acetate is the type of membrane material that has been available for the longest period. The second type is polyamide, and the third and most recent material, is a thin film composite. Each membrane has certain feed water requirements that must be adhered to if normal membrane life is expected. The factors that most often affect membrane material are as follows: pH, temperature, bacteria, free chlorine, and Langlier saturation index. Most of the factors listed above should be easily understood with the exception of Langlier saturation index. This is the measure of the scaling the exception of Langlier saturation index. This is the measure of the scaling tendency of a particular water source. In most cases, Langlier index is calculated and considered positive or negative. When calculating the Langlier index, certain feed water components must be measured. They are as follows: water temperature, total ionized solids, calcium hardness, alkalinity, and pH. If the index is positive, the feed water is considered to show a high potential for scaling and subsequent membrane damage. If this is the case, pretreatment is warranted. Chart No. 1 (below) shows the most common contaminants found in portable water and their limitation for the individual membrane material. Cellulose acetate has largely been replaced by polyamide type membranes.

CHART 1

	Cellulose Acetate	**Polyamide**	**Thin Film Composite**
pH	4-8	1-11	1-11
Langlier Index	Negative	Negative	Negative
Free Chlorine	0.2-1 .0ppm Of Free Chlorine	0-0	0.0-1.0ppm or 500 ppm days
Bacteria	Required Chlorine affected by Bacteria	Not affected	Not affected
Temperature	4-30°C (40-86°F)	4-30°C (40-85°F)	4-30°C (40-85°F)
NOTE: Product water volumes are affected by feed water temperature for every 1°C below 25°C a 3% decrease in the product water volume will be realized. *ppm days = In 1 ppm free chlorine feed water, membrane will operate 500 days before difficulties will exist.			

There are many feed water contaminants that can affect reverse osmosis membranes, such as silica and iron, but the previously listed five classes constitute the majority. Resulting from the feed water limitations of reverse osmosis membrane materials, a percentage of the systems require some form of pretreatment to maximize the useful life of the membrane. The most common form of pretreatment is softening. By exchanging the hardness ions in a particular water supply with sodium, the scaling tendencies of water are reduced, thus correcting for a positive Langlier index.

If pH adjustment is required to correct for a high feed water pH, then acid injection is warranted. Normally sulfuric acid is injected into the incoming water stream in a metered amount to affect the needed pH change. This is normally accomplished by converting alkalinity to carbon dioxide.

Bacteria affect some membrane materials and others are resistant. Cellulose acetate membranes are affected by the presence of bacteria. If a water supply is not sufficiently chlorinated to prevent bacterial damage, then chlorine must be added. Certain membranes are not affected by bacteria but cannot tolerate the presence of any oxidizing agents. If this is the case, then incoming water must be treated to remove the potentially damaging component. Carbon is most often used for pretreatment. While carbon is effective at removing chlorine, it may not remove other oxidizing agents that may be present. For this reason, sodium bisulfate injection is often used in place of carbon.

Up to this point, we have discussed how the chemical make-up of water affects the reverse osmosis membrane. Now we'll explain briefly how physical properties, most notably temperature and pressure affect the reverse osmosis system operation. Feed water temperature has a marked effect on the quantity of water a particular membrane is capable of producing. Membrane performance is based on a feed water temperature of 25^{o}C (77^{o}F). For every 1^{o}C below 25, a 3% reduction in quantity of the water the membrane will produce will be realized. For this reason, temperature adjustment of the feed water is often recommended. Temperatures above 35^{o}C (95^{o}F) will damage most membranes.

Incoming water pressure affects both the quality and quantity of water produced by the reverse osmosis system. Although pressures up to 400 PSI and beyond will not damage membranes, low operating pressures will reduce the effectiveness of a membrane to remove impurities. Reverse osmosis systems operating at 100 PSI will improve the quality 5-10%, as compared to operating at 60 PSI. Below 50 PSI, the quality is more drastically affected. The quantity of water produced will also be affected by pressure. Simply put, the lower the pressure, the lower the amount of product water produced. In summary, the softening process exchanges sodium ions for multivalent ions, deionization removes all the ions and the Reverse Osmosis removes the organics as well as the ions.

Conclusions:

When a plant experiences lithographic problems due to water quality, some form of water treatment is indicated.

The choice of the treatment process is governed ultimately by the economics and the applicability of the treatment process in solving the particular problems being encountered.

A trial period of use with the selected treatment method and optimized fountain solutions and ink formulations is highly recommended to assure good performance in any given pressroom with the new water source.