Honorable Discharge: Decolorization of Natural Fabrics

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Discharge is the removal of a dyed color. I must admit that the logic of intentionally coloring a piece of cloth, then taking the color out can seem elusive. There are some logical answers; you can achieve dark, rich background colors in printing and resist dyeing that are not achievable by printing large areas a solid color or overdyeing. But the real answer is that there is a magic in the discharging, similar to that of the raku process in ceramics. You dont just discharge navy blue to white every time. First you get a range of colors from navy to white and there might be traces of turquoise or violet too. If you heavily discharge you can get predictable results, but I love to do discharge gently and slowly and produce as many colors as possible. Dyes that discharge to another color are very intriguing. I also like the aged or ageless appearance of the partially discharged colors. But the magic is most evident when you do it, so try some simple projects to see if you can find magical colors by discharging.

Discharging and Bleaching

The concepts of bleaching and discharge are intertwined and confused. Both processes remove color and use some of the same chemicals, but there are some significant differences. Bleaching is commonly used to describe the removal of unwanted color in new fibers or cloth, most often to produce white. The final step in a weaving mill producing white linen is bleaching. Discharge is the removal, partial or complete, of a dye color. The term color stripping is sometimes used when the complete removal of a dye color is executed. Discharge printing is used to lift out circles of color from a navy cloth to produce white polka dots on a navy ground

Changing the Color of the Dye

How can you change the color of a dye molecule? Is this even a reasonable question? We have all seen molecules change color when we use indicator paper to test pH. The dye molecules impregnated into the paper change color in response to the acidity of the solution; that is when the molecules either lose or gain hydrogen ions. So the underlying principle is that if you change the molecular structure of the dye you will probably change its color. Most molecules are colorless. So if we change the structure of a dye molecule we have a very good chance that the new one will be colorless, so most dyes discharge. But not all dyes will discharge, so test a sample before you undertake a big project. In a family of dyes some colors may discharge and others wont. In the fiber reactive dyes Cibacron F, of the 6 colors I use only 4 will discharge; the gold and bright blue will not. So if I want a Cibacron F black that will discharge I will leave gold and bright blue out of the formula. Sometimes a dye just changes colors under discharge conditions. The Lanaset violet discharges to yellow, a lot more fun than dirty white.

Common chemical ways of modifying the structure of a molecule are oxidation and reduction. Oxidation is the addition of oxygen to a molecule, and reduction is the removal of oxygen from a molecule. There are discharge reagents that work by oxidation and others by reduction. Oxidation methods are familiar to everyone who has bought a bottle of bleach. Reduction processes produce less fiber damage, consequently there are more reducing discharge reagents.

The Oxidizing Reagents

An old but still common method of bleaching is sun bleaching. Many acres of fields in Ireland were dedicated to the sun bleaching of linen before the discovery of chemical bleaches. The first, *eau de javel,* was a weak solution of chlorine in water. Bleaching linen chemically allowed the bleaching fields to be used for potato cultivation and to improve the amount of foodstuffs available to the humble people but at the same time many workers in the bleach houses were dying from the chlorine. It was progress at a price.

Only cellulose fibers will sun bleach without substantial fiber damage. This illustrates two themes in discharging and bleaching: 1) cellulose and protein fibers react differently and 2) these discharge reagents can damage the fibers.

The Chlorinate Bleaches

These are common laundry products such as bleaches and bleaching powder. They are hypochlorite bleaches; the liquid is an alkaline solution of sodium hypochlorite, NaCIO, and the powder is calcium
hypochlorite, Ca(CIO)2, both decompose and give off chlorine gas, which is the active ingredient. Industrially chlorine and chlorine dioxide, both gases, are used to bleach cloth and paper. All give off chlorine gas which is very poisonous, as the original Irish workers discovered.

These whitening agents can only be used on cellulose because they damage wool and silk. Even cotton must be bleached with chlorinated agent with care because at the same time the chlorine is reacting with the dye molecules it is also reacting with cotton. This competing reaction always occurs so the trick is to get the dye discharged before too much damage is done to the fibers. The bleaches work over a range of pHs, from pH 5 to pH 9. But at a pH 7 the reaction with the cellulose is faster then the reaction with the dye, so working at higher or lower pHs protects the fibers. All the bleach should be removed from the fibers at the end of the decolorization to prevent further damage. Rinsing and washing help but there are some chemicals that will remove all the traces of residual chlorine; sodium bisulfite and hydrogen peroxides.

Safety

Many people think that because they can buy bleach in the supermarket it is safe to use and they feel more comfortable with bleach than with alien sounding thiourea dioxide. It also works at room temperature, making it easy. Friends have told me they like the smell of chlorine, it smells clean. Well it doesnt smell clean to me, it smells dangerous. I have a friend who discharge printed many pieces for a conference in her basement. She used bleach instead of thiourea dioxide, which she had used previously, because a journal insisted that thiourea dioxide was too dangerous to use. At the end of the discharge printing session she had a burning sensation in her nose and throat and in a few days she had severe bronchitis. I dissolved black cotton yarn in household bleach in my first discharge project (the goal was to get the black out).

Chlorine and chlorine based bleaches are dangerous to you, to everyone else who breathes the fumes, to the fiber and to those who manufacture the bleach. These strong oxidants will react dangerously with other common chemicals such as ammonia (read the bottle). It is an environmental hazard because chlorine is so reactive it reacts with other compounds to make new chlorinated products, many of which are on the hazardous disposal list. Bleaching paper (also cellulose fibers) with chlorine produces dioxins, a persistent and ultratoxic byproduct that is accumulating in our biosphere. Most paper mills have changed to peroxides or sulfur based bleaching processes due to pressure by Greenpeace.

If you must use chlorine based products and you want to protect yourself from the fumes with a mask, you must have cartridges for chlorine or acid gases; organic vapor cartridges will let the chlorine pass through. If you can smell it the chlorine is already damaging your mucous membranes.

The Peroxides

Hydrogen peroxide (used to bleach hair) is an oxidative bleach gentle enough to be used on protein fibers such as hair, wool and silk, as well as on cellulosic fibers. It decomposes directly to oxygen and water, which are not toxic compounds. Hydrogen peroxide comes in different concentrations, 3% and 30% are the ones of interest to us. The 3% solution can be purchased in drug stores and it is often used to kill germs in minor injuries. It can be used to remove traces of chlorine bleaches or stains on silk or wool. The 30% solution will bleach hair and some dyes. Because it is a mild reagent it may take a long time to decolorize dark hues.

Other peroxides are white solids and used in some bleaches that are chlorine free. Hydrogen peroxide is used to bleach tussah silk. It takes process for 2-6 hours at 71° C (160° F). It is also used as an alternative to air oxidation of vat dyes, being faster and more controlled.

Safety

Hydrogen peroxide is active at room temperature but reacts faster at higher temperatures. This means that the bottle also reacts sitting on the shelf, so you should check potency before using an old bottle. The only hazard I know from hydrogen peroxides is the rapid decomposition of concentrated solutions over 30%; in fact, so rapid that it explodes. Stay away from such concentrated solutions. No inhalation protection is needed.

The Reducing Agents

All these agents change the structure and hence the color of a dye molecule by chemical reduction. The first of these reagents was sulfur. Wool was whitened by burning yellow sulfur in the room. When you burn sulfur you produce sulfur dioxide, SO_2, a gas which is what actually reacts with the wool. Sulfur dioxide is a gas with a pungent, acrid smell that is also famous for its role in acid rain. The noxious sulfur smell we associate with rotten eggs and skunks is from a different family of sulfur compounds derived from H2S. These H2S based compounds are also more of a health periI.

All reducing discharge reagents work by producing the same sulfur dioxide; they are compounds that under specific conditions slowly decompose and release sulfur dioxide that then reacts with the dye. This slow release in solution is a very effective way to 1) make contact with all parts of the textile and 2) use up all the sulfur dioxide before it escapes into the air.

The sulfur dioxide reacts with the dye molecules, not the fiber, so can be safe for use on all fibers: wool, silk, cotton, etc. These compounds are also used as the reducing agent with vat dyes including indigo.

Dyes that react or discharge with oxidative reagents may or may not discharge with reductive agents. Dyes that do not discharge with bleach may discharge with these reducing discharge reagents. The color of an oxidative discharge is generally different from a reductive discharge color. But all the reducing discharge reagents will produce the same discharge colors.

The greatest personal hazards of these discharge reagents is from inhaled gases or fumes. Work in a well ventilated area, such as the great outdoors. This also protects others who are not discharging. In a closed space or if you work over the pot, wear a mask with acid gas cartridges. Wearing a mask with organic vapor cartridges will not protect you from the SO_2 and H_2S released by these discharge reagents.

Hydrosulfite

Sodium hydrosulfite, sometimes called hydro, is the first of these compounds developed and is still the cheapest and thus used extensively by industry. Sodium hydrosulfite is a white solid that readily decomposes under alkaline conditions, even at room temperature. It is the active ingredient in color removers you can buy at the supermarket.

Safety

Sodium hydrosulfite is so reactive as a solid that it can react with the air and humidity. This has two unfortunate consequences; 1) the solid is flammable and 2) the shelf life is short.

The flammability of the solid is such that it may burst into flames in contact with hot water (definitely a fire fighting hazard). This makes it a hazard to transport and store. If you do have some on the shelf it reacts with air and humidity and quickly loses its potency. It also forms many H_2S compounds as byproducts.

I think these risks make sodium hydrosulfite unsuitable for use in a studio, especially since lower risk alternatives are available.

Thiourea dioxide

Thiourea dioxide is a discharge reagent familiar to industry, crafts and studio artists under many trade names: thiox, TUDO, Monofest and Spectralite. It was developed in the 1940s in

England as an improved or stabilized hydrosulfite. It is a non-flammable white solid with a long shelf life (keep it dry). Thiourea dioxide is also 5-7 times stronger than sodium hydrosulfite but more expensive. A safer discharge can be effected by substituting 20g of thiourea dioxide for each 100g of sodium hydrosulfite.

Under alkaline conditions, i.e. in the presence of soda ash (Na_2CO_3), hot solutions of thiourea dioxide decompose to urea, sulfur dioxide (the active reagent), urea and salts. Thiourea dioxide is active under a wider range of alkaline conditions than hydrosulfite. At room temperature solutions are stable for several hours. Temperature can be used to control, stop or accelerate, the discharging.

Thiourea dioxide is used extensively in vat dyeing, discharge printing and color stripping. The conditions for discharge can be gentler for fibers that do not like alkaline conditions such as silk and wool. These fibers can benefit from a final soak in dilute vinegar to neutralize any residual alkali.

Many recipes for discharging with thiourea dioxide exist; typically they contain thiourea dioxide, soda ash as the alkali and must be heated. A boiling solution loses its ability to discharge quickly, say in 30 min. So you can reheat discharge solutions but you may need to add more reagents too. I like to discharge gently and slowly, going through many colors on my way to white. In fact I usually do a partial discharge, if Im careful and lucky I can get all the discharge colors in the piece. Also, discharge is irreversible; you can always discharge some more but when the color is gone it is gone. But if you want white polka dots on black you can hit it hard.

Thiourea dioxide is used for:

Discharge printing. A print paste is made by mixing and dissolving thiourea dioxide and soda ash in a thickener such as alginate. Other common print paste additives such as urea may make the paste behave better for your application. The paste can be stamped, silk screened, brushed.... on to the cloth. When the print paste is dry (to prevent smearing) the discharge process is accelerated by heating: steaming, ironing or the dryer. The discharge paste is good for about 1/2 day or until it turns all bubbly.

Immersion discharge. A bath large enough to cover the fiber is prepared with thiourea dioxide, soda ash and possibly a leveling agent and heated . The fibers can be introduced when the bath is cold or hot depending on your goal. For color stripping or color correction introduce the fibers in the bath and heat and move the fibers in the bath (highest temperature is limited by the fiber). For discharge *shibori,* bring the bath to a boil, add the reagents then introduce the wetted out resisted cloth or pour the boiling solution over the piece. The discharging can be stopped by plunging the cloth into cold water. This gives you a chance to look at it and see if it is discharged enough, if not you can return it to the bath and discharge more. If nothing happens to the color in say 10 min, then remove the cloth and add more reagents in the same proportions and then return the cloth. Some dyes require much stronger solutions to discharge.

Cleaning. Left over discharge baths or print paste dissolved in hot water can be used to restore discolored equipment or utensils. Just pour the solution in, cover, and let soak. Fresh solutions can be made for a special case and they can be heated too.

Safety

Thiourea dioxide is not a significant health hazard. Most of the transportation and storage hazards are gone, but if it is mixed with an oxidizing agent it could react violently (same for hydrosulfite). You need to protect from the gases by having good ventilation and/or wearing a mask as discussed before.

I have made extensive searches for toxicity of thiourea dioxide and its decomposition products and have found very little published and all of the risk is associated with the sulfur dioxide formed. But thiourea dioxide has gotten a toxic reputation from its similarity in name to thiourea, a probable human carcinogen. Despite its name (actually a misnomer, chemical name sodium dithionite) it does not contain or decompose to thiourea.

The spent reagents should be disposed of in the sewer system.

The sewer system is designed for just such events and the amount you are introducing is small. Septic systems are a different bird and there are no studies to give us facts but you could let the solutions set overnight to consume all the thiourea dioxide and then neutralize the alkali with vinegar before adding to the septic system.

Sodium Formaldehyde Sulfonxylate

Sodium formaldehyde sulfonxylate is sold under the such trade names as Formosul, Safolite and Rongalite C. It is an older stabilized variation of sodium hydrosulfite. It is a white solid with a long shelf life very much like thiourea dioxide. It differs from thiourea dioxide in two ways: 1) it heats spontaneously when in contact with water so must be kept dry, 2) it works under acid as well as alkali conditions. For textiles sensitive to alkali this can be helpful. Beware that under acid conditions more of the H2S type byproducts will form and the smell will be more noxious. It also works at slightly lower temperatures than thiourea dioxide, but I have never used this feature.

Safety and disposal are the same as for thiourea dioxide.

Glossary

Alkali A substance that creates an alkaline or basic solution, pH>7.5. Common alkali used in dyeing are baking soda, soda ash, washing soda and lye.

Baking soda Sodium bicarbonate, sodium hydrogen carbonate, NaHCO3. A very mild alkali.

Bisulfite Sodium bisulfite, sodium hydrogen sulfite, NaHSO3, Anti-chlor concentrate. A white salt used to react with residual chlorine in the fibers and thus protect them from further damage.

Bleach An alkaline solution of sodium hypochlorite or solid calcium hypochlorite, laundry bleach, bleaching powder. An aggressive chlorine based oxidizing agent that can remove color and damages the fiber.

Hydrogen peroxide Oxygenated water, H_2O_2. A mild oxidizing agent that can remove color even on protein fibers.

Hydrosulfite Sodium hydrosulfite, sodium dithionite, hydro. A reducing agent widely used in vat dyeing and discharging. It is the active ingredient in store bought color and rust removers.

Soda ash Sodium carbonate, Na_2CO_3. Dissolved in water it creates a mild alkaline solution or it raises the pH.

washing soda Sodium carbonate decahydrate, $Na_2CO_3.10H_2O$, sal soda.]ust a different crystalline form of sodium carbonate.

DISCHARGE RECIPES

Immersion discharge.

Use a stainless steel or enamel pot , fill with enough water to allow the submerged cloth to move freely. Add

1. a drop of Syntrapol (surfactant)
2. 1 teaspoon of soda ash
3. 1 teaspoon thiourea dioxide.

Begin heating, when the soda ash has dissolved you may add the cloth. Stir and watch. Remove the cloth when it seems to be the right color. To stop the discharging, plunge the cloth into a bucket of cold water. You may put the cloth back into the discharge solution to remove more color.

The solution will lose its ability to discharge in about 1/2 hr. Some dyes will not discharge until you have added 2 tablespoons each of soda ash and thiourea dioxide.

Discharge print paste.

Prepare sodium alginate or a commercial print paste ahead of time. They take a while to hydrate and keep well. Dilute this gel to the right consistency for your method of application. When in doubt , use the paste just as you made it. To 1/2 cup of the prepared paste add 1/2 teaspoon soda ash and 1/2 teaspoon thiourea dioxide and stir until dissolved (no white lumps or grains), this will take a while.

Test to see if you have an effective concentration for your dye and project. Dab a bit of the discharge paste on a corner or sample of the cloth and heat with a hair dryer or heat gun. If the cloth does not discharge you can add more soda ash and thiourea dioxide, 1/2 teaspoon at a time, until it works.

Print, silk screen, paint, roll or daub the paste onto the surface of the cloth. If it is a small area you can heat immediately with a hair dryer or heat gun. Otherwise allow to dry before moving the cloth (to avoid smearing the paste) Once it is dry you can steam it, throw it in the dryer (easy to monitor because you can stop the dryer and see the color change) or cover with some paper and heat with the iron (also easy to monitor the color change).
The discharge paste will generally work for 1/2 a day. Discard when it gets all foamy.

Project

This project combines printing with shibori inspired resists. The starting cloth is a heavy weight silk noil commercially dyed black. The cloth has to be heavy enough to keep the print paste from bleeding through to the back side of the cloth. Lay the cloth out on a print table and randomly pleat and tuck the cloth until only 2/3 or so of the surface of the cloth is visible. Many little tucks work better than a few large ones. Now iron it in place to flatten the surface for printing. A few straight pins around the edge and in some of the pleats will make it easier to print. For the piece shown, I printed with a hand carved wood block from India, a rectangular scrap of wood and a wooden dowel with some moleskin on the tip. I crated a stamp pad with a thin piece of foam on a plate, added some print paste and stamped the entire surface with the 3 wood blocks. Let the paste dry, cover with newspaper and heat with the iron. The color you see initially includes the color of the print paste. After heating, wash to remove the print paste and add some vinegar to the final rinse to neutralize the soda ash.