CHEM 470
The Science of Reactive Hair Care Products

A review of changing natural hair appearances

I. Permanent Waving
   a. Modern society - The biological purpose for having hair has been surpassed by its purpose in fashion
   b. 1900s – waving achieved by heating hair with electrical devices
   c. Past 50 years, chemical techniques to impart lasting wave or curl to hair
      i. Permanent waving or perming
      ii. “permanent” – only affects existing hair
      iii. As new hair grows out of the scalp, it will grow in its original configuration
      iv. Different forms
         1. acid, cold or neutral waves
         2. thioglycolates and bisulfites
   d. How permanent waves work: it should be known that the science of reactive hair products is very involved – this is only an introduction for the uninitiated chemist
      i. Hair is composed of helical protein structures crosslinked by sulfur-sulfur bonds
      ii. These bonds are responsible for hair structure, and they can be disrupted by reducing reactions (simplified)
      iii. Thioglycolic acid and bisulfite derivatives
      iv. Since 1940s
      v. Combining these ingredients with reactive agents and with other ingredients to control pH and viscosity
   e. The process: first step is to physically rearrange the original configuration of the hair on curlers or rods
      i. The size of the rod determines the size of the curl
      ii. The thin sheets of tissue paper, known as “end wraps” help the hair hold the proper configuration and protect the ends by absorbing excess perming solution
      iii. When the perming solution is placed on the hair (after rolling) the bonds of the hair break (reaction time depends on perm solution, restructuring of the hair and condition of the hair)
      iv. The hair is quenched with water to stop the reducing reaction
      v. A neutralizing solution is added to oxidize the protein residues, and relinks the sulfur-sulfur bonds in a newly arranged configuration
      vi. Protein kinetics, ET Borish, Hair Waving, Hair and Hair Care Marcell Dekker, 191-215 (1997)

vii. Damage results when the disulfide bonds are broken and swelling ensues
viii. Swelling results from exposure to the highly alkaline materials and can cause significant cross-sectional or lateral damage
1. Damage can also result when treating improperly wrapped hair with a reducing solution

f. Permanent wave formulations: Generally perm solutions contain a number of ingredient classes (table 1)
i. Three types of perms: alkaline, acid and bisulfite
ii. Alkaline perms, also known as cold waves use thioglycolic acid
1. the name (alkaline) is derived from the final pH of the product
2. alkaline perms typically have a pH greater than 9
3. another subcategory is the exothermic perms that rely on HOOH to generate heat by oxidizing thio in situ – "self-timing" perms
iii. Acid perms made with glyceryl monothioglycolate
1. thioglycolic acid derivative that is effective from pH 7-8
2. even thought the pH is neutral, these perms have been known as "acid perms" in comparison to their higher pH cousins
3. perceived to be less damaging
iv. Bisulfite perms were designed for mildness
1. hydrogen bisulfite rather than thio derivatives
2. reacts at a lower pH than thioglycolic acid, so there will be less swelling and less cuticle damage
3. the reaction between bisulfite and keratin may form what is known as a Bundte salt
4. because of the salt formation, it is difficult to react the sulfo groups to reform all of the disulfide bonds
a. bisulfite perms can leave hair physically weaker
i. softer, less stable perm
ii. still popular in the marketplace because they are less aggressive and can be used at a lower pH

II. Hair Relaxers
a. Straightening excessively curly hair
b. Typically used on African hair which is significantly curlier than Caucasian or Asian hair
c. Structure of African hair is more elliptical and varies more in diameter
d. Can be done chemically or mechanically

e. How relaxers work: similar to permanent waves – rely on breaking S-S bonds
    i. Lanthionization – conversion of cystine to lanthionine
    ii. Based on metal hydroxide
    iii. First add protective cream (pet. Jelly) to hair line, ears and the ends of the hair
    iv. Cream relaxer is brushed on section by section
    v. 10-20 minutes processing time
    vi. Rinsing thorough
    vii. Some relaxers do not require an oxidation step, it is common to shampoo the hair with a neutralizing shampoo immediately after relaxing
    viii. Additional conditioning step
f. Relaxer formulations: since 1950s there have been many varieties
g. Three key components
    i. Water-soluble/water-dispersible alkaline agent, oil phase and water phase
    ii. Lye relaxers contain between 1.85-2.4% sodium hydroxide

III. Oxidative Hair Color
a. Some coloring involves reactions with the natural pigments of hair
    i. Oxidative or permanent hair coloring
b. Two melanin-based pigments affect natural hair color
    i. Eumelanin, which is responsible for blond, gray, brown and black shades
    ii. Pheomelanin, which produces reds and yellows
        1. these same pigments can be found in squid ink, bird feathers, and various mildews and molds
c. During oxidative coloring, color is produced inside the hair shaft from aromatic amines and phenols reacting with HOOOH; the resulting hair color is “locked” inside the hair shaft
    i. Repeat about every 30-45 days as new hair grows
d. How permanent hair color works: Oxidative dyes are small, colorless molecules that penetrate the cuticle and pass the cortex
e. These reactive species are then oxidized to form larger molecules that combine with other additives, known as couplers, to form various colors
f. The resultant polymers, too large to pass out of the hair again, are essentially permanent
g. Process occurs under highly alkaline conditions, which swell the hair, allowing better penetration of the dye precursors
h. The high pH also increases the oxidative reactivity of HOOH and promotes rapid lightening and color formation
i. Lightening the original hair color is possible because HOOH will destroy some (or much) of the existing natural pigments in the hair
    i. Allows hair to achieve a color that is lighter than its original state

j. Several steps: must first test to make sure it is safe for skin
    i. First: the peroxide and tint are mixed together in applicator bottle
    ii. The tint is then applied from the scalp to the porous ends
    iii. 10-20 minute reaction time
    iv. Rinse
k. The color imparted to the hair depends on concentrations of dye and peroxide, processing conditions, condition of hair
    i. Hair should not be colored before perming (could chemically alter color)
l. Permanent hair color formulations: Permanent dye formulations consist of two components that are separate until the product is ready to be applied
    i. #1: Oxidative dye precursors, *p*-diamines or *p*-diaminophenols, *p*-phenylene diamine
        1. colorless precursors
    ii. form dye intermediates, which react with dye couplers to produce color
    iii. may contain five or more dye precursors
    iv. an alkali is used as part of the dye base to swell the hair and enhance penetration of dye precursors
        1. may include solvent, surfactants, thickeners and metal chelating agents
    v. #2: HOOH and stabilizing agents
        1. two components are mixed together just before use to initiate reactions that will form the permanent dyes
    vi. regulatory and toxicological considerations extremely important
    vii. short-term effects: contact dermatitis

Table 1. Permanent Wave Ingredients

Reducing agents	Thioglycolic acid, thiolactic acid, glycerol sodium sulfite
Wetting agents	Sodium lauryl sulfate, disodium laureth sulfosuccinate, sodium laureth sulfate, cocoamphodiacetate
Buffering agents	Ammonium carbonate
Conditioning agents	Keratin hydrosylate, collagen hydro-sylate
Oxidizing agents	HOOH, potassium bromate
Stabilizers	Citric acid, sodium stannate
Ancillary agents	Various emulsifiers, thickeners, fragrance