Colorants

Pigments versus Dyes

Colorants — impart color

- Pigments — insoluble colorants
  - usually inorganic compounds
- Dyestuffs — soluble colorants
  - usually organic compounds
- Lakes — soluble dye attached to inert support
  - Used as pigments
- Fillers —inexpensive insoluble materials
  - Can be organic or inorganic compounds

Brief History of Colorants

- Before the Industrial Revolution…
  - Early pigments
    - ground colored minerals
      - Fe_2O_3, HgS, As_2S_3
  - Early dyes
    - extracts from plants and animal sources
      - Madder root, Indigo leaves, snail and insect secretions

Brief History of Colorants

- After the Industrial Revolution…
  - Synthetic pigments — 1704 “Prussian blue”
    - Followed rapidly by…
      - Synthetic ultramarine
      - Cobalt blue
      - Cadmium reds and yellows
      - Chrome oxide green (Army green)
  - Synthetic dyes — 1856 — “Mauve of Mauvine”
    - Followed by…
      - Synthetic Indigo
      - Synthetic diazo dyes in every color imaginable

Artists' Palettes Through the Ages

	Red	Yellow	Green	Blue	White	Black
Cave painting 10,000 BC	Ochre Fe_2O_3	Ochre Fe_2O_3	—	—	Chalk ($CaCO_3$) Gypsum ($CaSO_4$)	Carbon (lampblack)
Egypt 1300 BC	Red lead Pb_3O_4	Orpiment As_2S_3	Malachite $CuCO_3 \cdot Cu(OH)_2$	Egyptian Blue $CaCuSi_4O_{10}$	Chalk ($CaCO_3$) Gypsum ($CaSO_4$)	Carbon (lampblack)
Pompeii AD 79	Vermilion HgS	Orpiment As_2S_3	Malachite $CuCO_3 \cdot Cu(OH)_2$	Egyptian Blue $CaCuSi_4O_{10}$	Lime $Ca(OH)_2$	Carbon (lampblack)
Renaissance 1400 AD	Vermilion HgS	Lead/Tin Yellow	Green Earth Complex iron silicate	Ultramarine Complex aluminosilicate Azurite $2CuCO_3 \cdot Cu(OH)_2$	Lead White $PbCO_3 \cdot Pb(OH)_2$	Carbon (lampblack)
Impressionists 1860 AD	Vermilion HgS	Chrome yellow $PbCrO_4$	Viridian Cr_2O_3	Cobalt Blue $CoO \cdot Al_2O_3$	Lead White $PbCO_3 \cdot Pb(OH)_2$	Carbon (lampblack)

Timeline of White Pigments

Lead white — $PbCO_3 \cdot Pb(OH)_2$ — basic lead carbonate Banned in US in 1972

Whiting — $CaCO_3$ — calcium carbonate

Industrial revolution

Lithopone — $BaSO_4$/ZnS

Chinese white — ZnO — zinc oxide

Titanium white — TiO_2 — titanium dioxide

Black Pigments and Fillers

- Available from ancient times
- Most black pigments and fillers are carbon-based
  - Lampblack
  - Carbon black
  - Bone black
  - Graphite

All contain **C**

Mars black — an iron compound $FeO \cdot Fe_2O_3$

magnetite

Timeline of Blue Pigments

Ultramarine — lapis lazuli (2400 B.C.)

Egyptian blue —copper silicate

Azurite — $CuCO_3 \cdot Cu(OH)_2$

Smalt — CoAsS, $CoAs_2$ (12th century)

Prussian blue (1704)

Cobalt blue — CoO (1802)

Synthetic ultramarine (1831)

Cerulean blue — CoO, SnO (1860)

Smalt

Industrial revolution

Ultramarine

Timeline of Green Pigments

Malachite — $CuCO_3 \cdot Cu(OH)_2$

Green Earth (terre verte)

Verdigris — $Cu(CH_3COO)_2$ (Rome)

malachite

Industrial revolution

Scheele's green — copper arsenate (1778)

Emerald green (1814)

Viridian — Cr_2O_3 (1859)

Cobalt green

emerald green

Timeline of Yellow-Orange

Iron oxides — ochre, umbers, siennas

Orpiment — As_2S_3

Litharge — PbO (400 B.C.)

Van Dyke brown — organic bituminous

orpiment

Industrial revolution

Naples yellow — $Pb_3(SbO_4)_2$—1758 (Italy)

Chrome yellow — $PbCrO_4$ — 1809

Cadmium yellow — CdS — 1829

chrome yellow

cadmium yellow

Timeline of Red Pigments

Vermilion — HgS — cinnabar (3000BC)

Red Ochre — Fe_2O_3 — iron oxide

Realgar — As_4S_4 — red-orange

Minium or Red Lead — Pb_3O_4

Red lakes — natural dyes on clay

Industrial Revolution

Cobalt violet — $Co_3(PO_4)_2$ (1859)

Cadmium red — CdS/CdSe (1910)

cobalt violet

Synthetic Inorganic Pigments

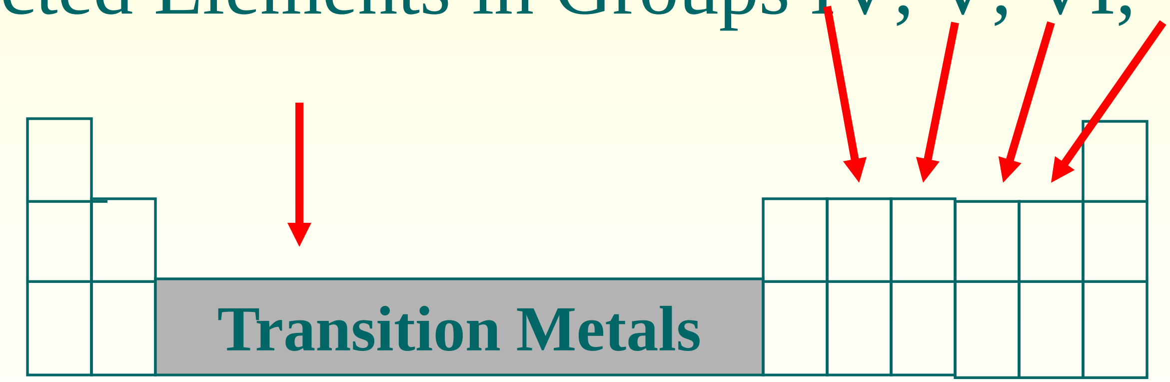
- commercial synthesis began in 19th century
- prepared by precipitation reactions
  - control of T, pH, mixing to insure uniform, desired particle size
  - purification of product and grinding
- brilliant colors, lightfast, heat stable, high tinting power

What Causes Color in Pigments?

What types of elements did you usually find in the chemical formulas of these natural and synthetic pigments?

Pigments and the Periodic Table

- Transition elements in Period 3
- Elements in Group IIB
- Selected Elements in Groups IV, V, VI, VII



Mechanisms of Inorganic Color

Two major mechanisms

- “d-d” electronic transitions
- Charge transfer transitions

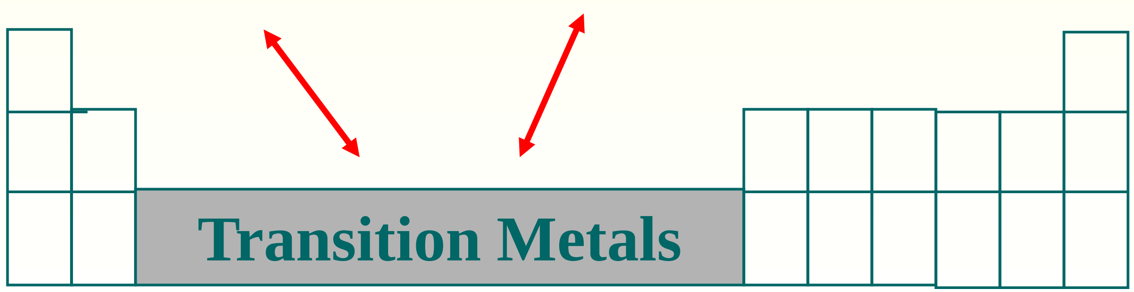
Electronic Transitions

- Energy is required for these transitions
- Light provides the energy
- Specific wavelengths (colors) of light energy are absorbed by molecules to allow the electronic transitions to occur.
- We see the molecules as “colored”.

"d—d" Transitions

- light-induced electronic transitions between energetically different d-orbitals
- compound must contain a transition metal with unfilled d-orbitals

Ti, V, Cr, Mn, Fe, Co, Ni, Cu



Pigments with Transition Metals

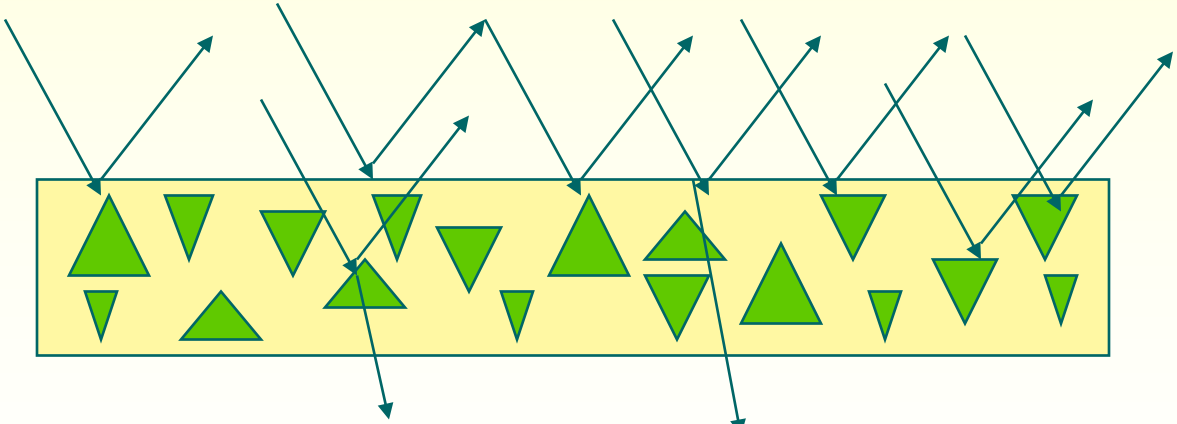
- Malachite and azurite — copper **Cu**
- Vermilion — mercury **Hg**
- Yellow ochre, red ochre, magnitite — iron **Fe**
- Cobalt blue, cerulean blue — cobalt **Co**
- Chrome oxide green, chrome yellow — chromium **Cr**

Ideal Properties of Pigments

- Lightfast — resists fading
- Chemically inert — resists oxidation
- Insoluble as possible — resists bleeding
- Good brightening or coloring power
- Uniform particles which can easily be dispersed in a binder
- **High opacity or hiding power**

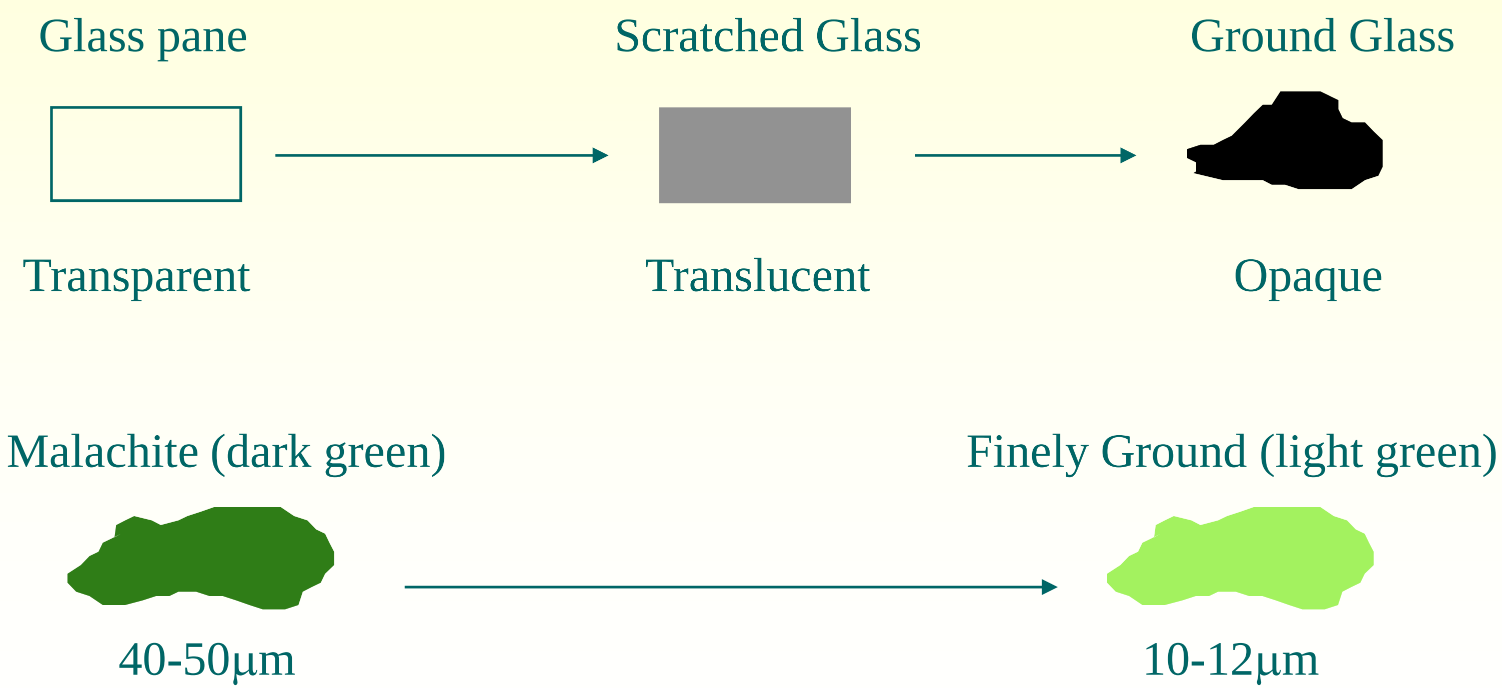
What Controls Opacity?

- The more a paint scatters light the more opaque it appears to be.



Light scattering depends on...

- Pigment particle size

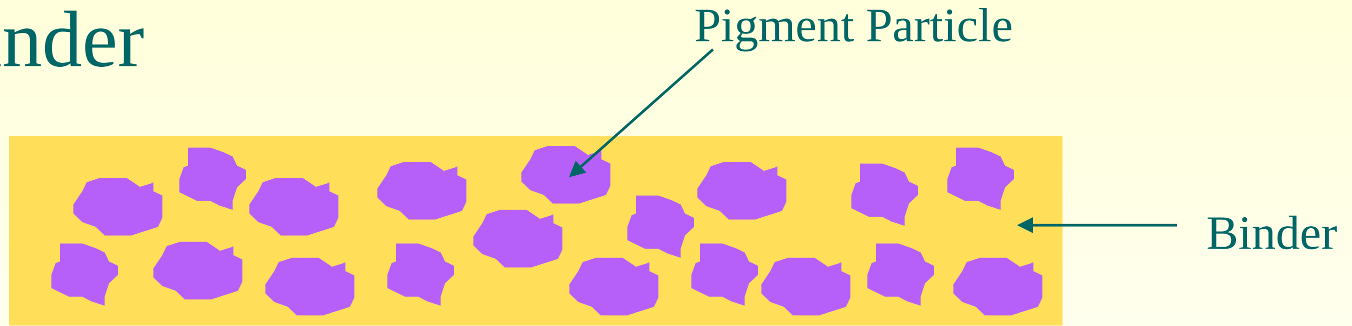


What is the best size?

- Most effective scattering
  - Particles in the 200 - 400nm range
  - 1/2 the wavelength of visible light (400-800nm)
- **smaller particle size = more scattering**

Light scattering also depends on..

- Refractive Index differences of pigment and binder



•If **RI** of pigment and binder are **different** = high scattering — **opaque**

•If **RI** of pigment and binder are **similar** = little scattering — **transparent**

•Higher RI means more bending of light in the medium.

Opacity and Refractive Index

Refractive Indices (RI)

Air	0
Binders	
Water	1.3
Linseed Oil	1.5
Pigments	
Chalk (filler)	1.6
Zinc oxide	2.0
Titanium dioxide	2.55-2.75

Chalk + water

0.3 difference

Chalk + oil

0.1 difference

TiO_2 + water

1.45 difference

Fillers in Paints

- Used to modify opacity or transparency
- Added to paint to
  - Thicken and change flow characteristics
  - Lower production expenses
  - Provide matte finish to dry paint
  - Prevent sedimentation or coagulation of pigments during production, transport and storage

Dye Definition

- Colorant which is homogeneously dispersed in the dye medium
- Usually soluble
- Naturally occurring or synthetic organics
- Categorized by...

1. Method of Application
2. Chemical Structure

But first….

Historical View of Dyes

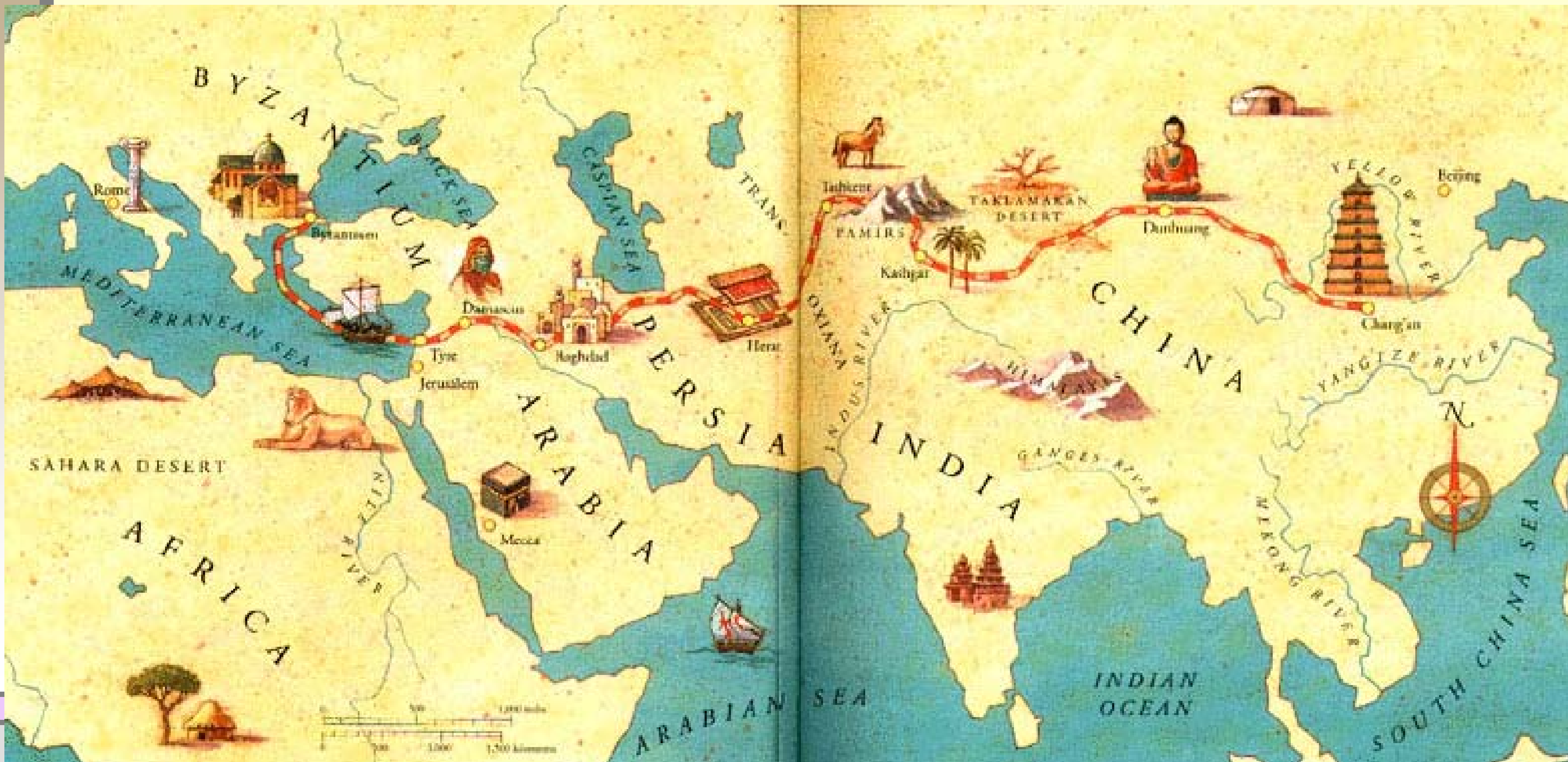
- Archaeological finds indicate dyes from natural sources have been used to color textiles for at least 6,000 years
- Dyeing became an established craft in India, China, South America between 4,000-3,000 B.C.
- Indigo-dyed garments from Thebes (ancient Egypt) — 2,500 B.C.
- Madder root dyed belt from King Tutankhamen’s grave — 1,352 B.C,

Exquisite Weaving and Dyeing

- Pazyryk carpet (Siberia) 5th century BC

- Peruvian textile 600-200 B.C.

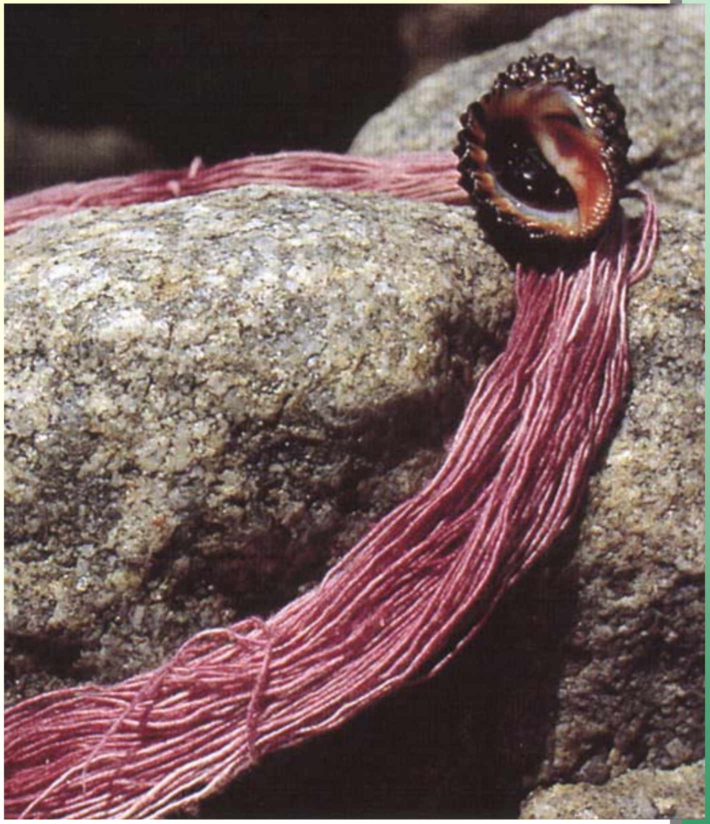
The Silk Road — from 2000 B.C.



Exchange of textiles, designs, ideas and **dyestuffs**

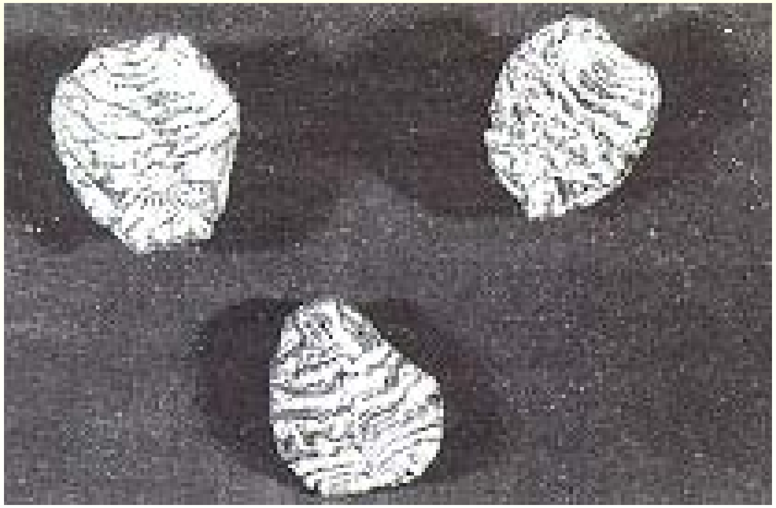
Dyes from Snails

- **Tyrian Purple** or "Royal Blue"
- 9000 snails to obtain 1 g of dye
- Used primarily before 8th century A.D. to dye wool and silk
- Chemically it is 6,6'-dibromoindigo

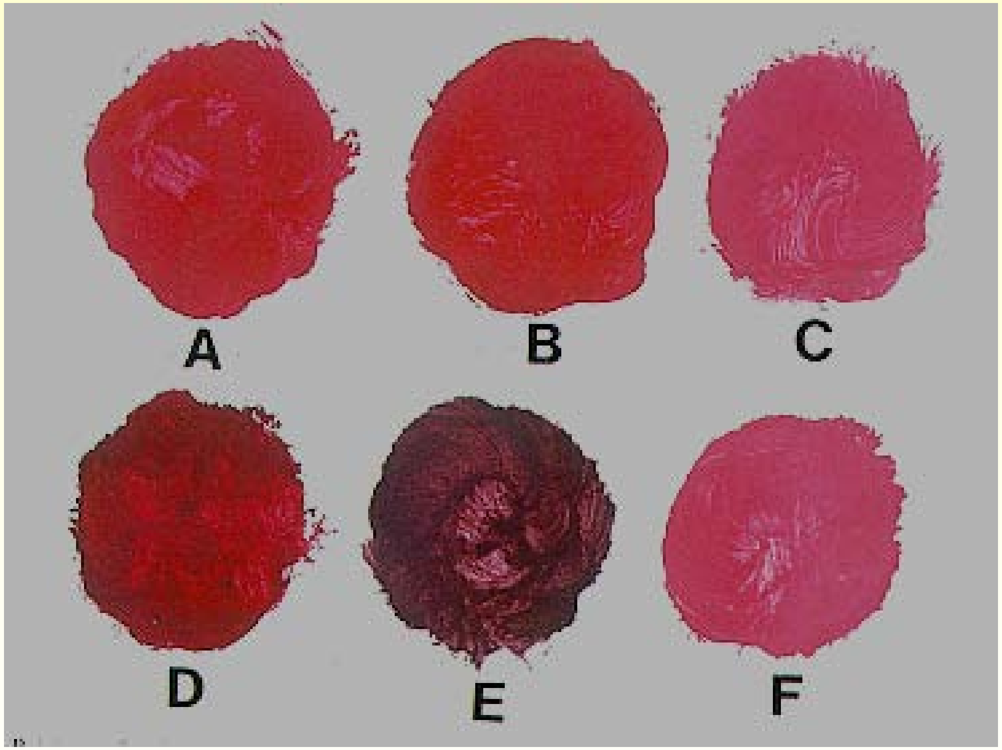


Dyes from Bugs

- **Kermes** — the most ancient dye in Europe
  70,000 female oak beetles produce 1 pound dye
- **Cochineal** — Mexico and Central America
  Mexican cactus beetle



Kermes, Cochineal — Carmine



Chemically similar structure, light sensitive

Dyed wool and silk — "carmine red"

Dyes From Plants

- **Indigo** — used since 2000 B.C.

  Extracted from *Indigofera tinctoria*

  “Navy Blue” of English sailors

  Blue jeans
- Insoluble in water
  - Must be chemical reduced to soluble ***leucoindigo*** to use as dye

Poor-man's Indigo

- **Woad**
  - Member of the mustard family
  - A common weed in temperate climates
  - Leaves contain same chemical as indigo but in lower amounts
  - Celtic war paint and tattoos

    Braveheart
  - Blue robes of priests

More Dyes From Plants

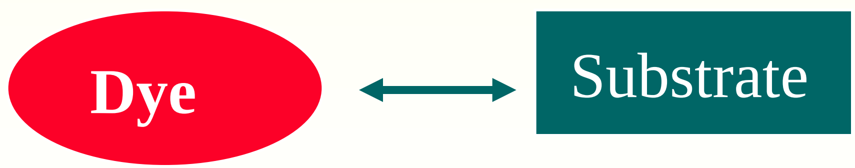
- **Madder** — "Turkey Red"
  - Root of madder plant found in Europe and Asia
  - Prepared as a "lake" with $Al(OH)_3$
  - British "Redcoats"
  - Alexander the Great used it to simulate blood

- Chemically — Alizarin and Pupurin

Synthetic alizarin prepared in 1875

Methods of Application

- Dye and Substrate can interact through...
    1. ionic forces (+ and — charges)
    2. hydrogen bonding
    3. van der Waals forces
    4. covalent bonds

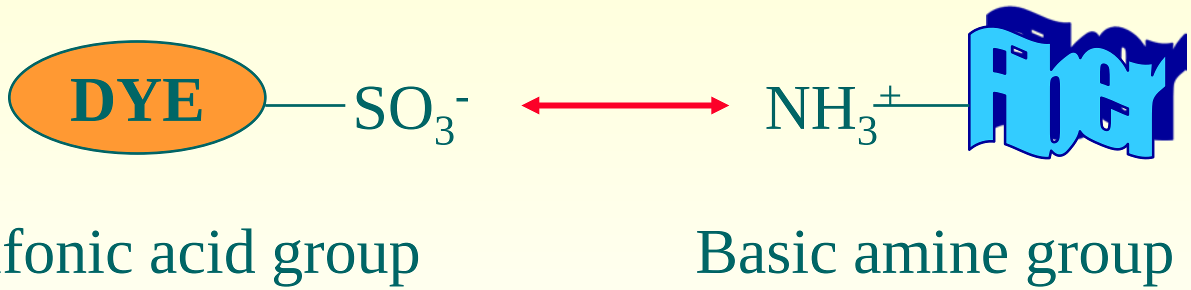


Types of Dyes by Application

- Acid Dyes
- Basic Dyes
- Mordant Dyes
- Direct Dyes
- Disperse Dyes
- Vat Dyes
- Fiber-reactive Dyes

Acid Dyes

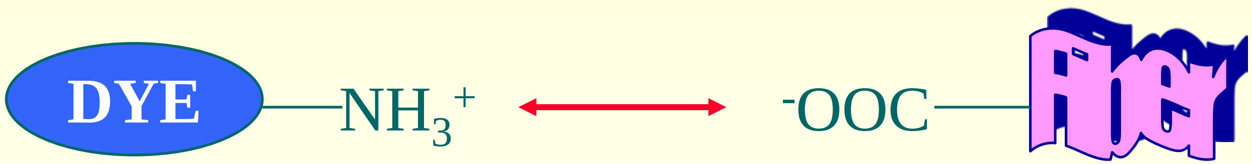
- Acidic dye (-) ⟷ (+) Basic fiber



- Wool, silk, nylon have amine groups

Basic Dyes

- Basic Dye (+) ⟷ (-) Acidic Fiber



Basic amine group Carboxylic acid group

- Wool, silk, leather, acrylic fibers have carboxylic acid groups

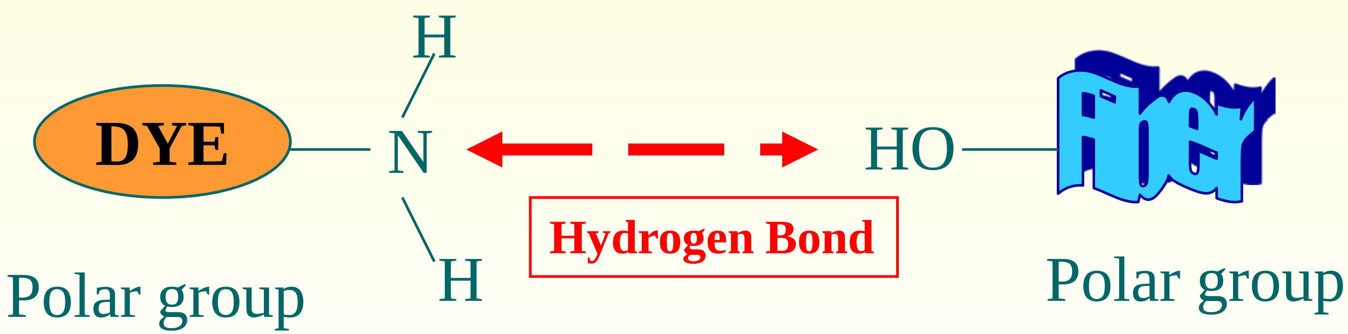
Mordant Dyes

- Have no natural affinity for fiber
- Must use a “mordant” to link dye and fiber

- salts of Fe^{2+}, Sn^{2+}, Cr^{3+}, and Cu^{2+}
- hydroxides of Al, Mg, Ca, and Ba
- tannic acid

Direct Dyes

- Polar dye ⟷ Polar Fibers
- Dye applied from a hot water solution



- Cotton and cellulose-based fibers
- Synthetic dyes

Fiber-Reactive Dyes

- Covalently bonded to fibers

  R—C—O—fiber

  R—C—S—fiber

  R—C—NH—fiber

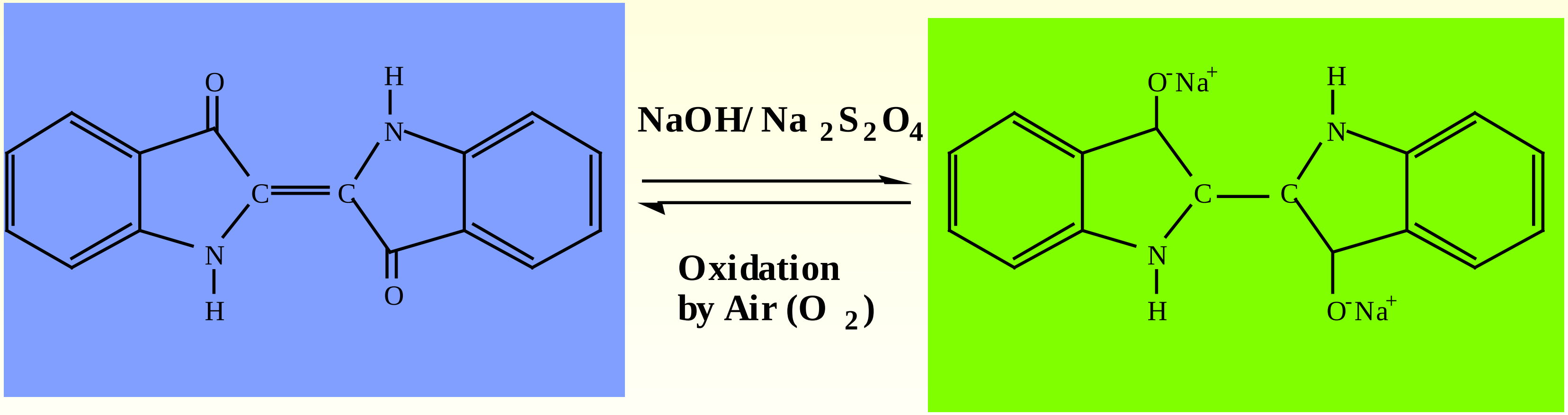
- Developed in 1950's
- Used primarily on cellulosic and protein fibers

Vat Dyes

- Usually not soluble in water
- Must be converted to a soluble form to be used as a dye

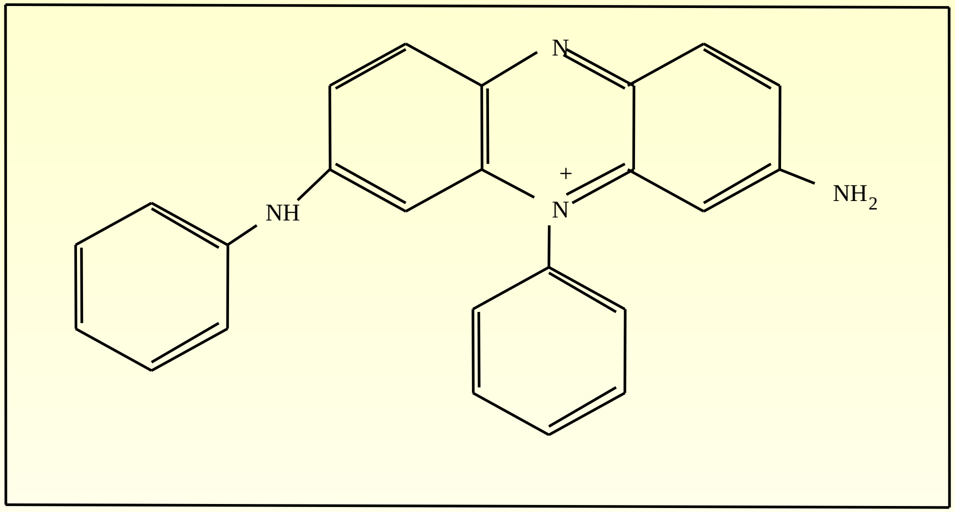
Indigo: the Classic Vat Dye

- Indigo is insoluble in water
  - Must be chemical reduced to ***leucoindigo***



- Leucoindigo is soluble
- Used to dye cellulose fibers — blue jeans

Mauveine — first synthetic dye



Conjugated Aromatic System of **Chromophores** and **Auxochromes**

AZO Dyes

- first prepared in 1863

  Have widest range of colors of all dyes

  Contain the **AZO Chromophore**

  Generally lightfast

R—N = N—R

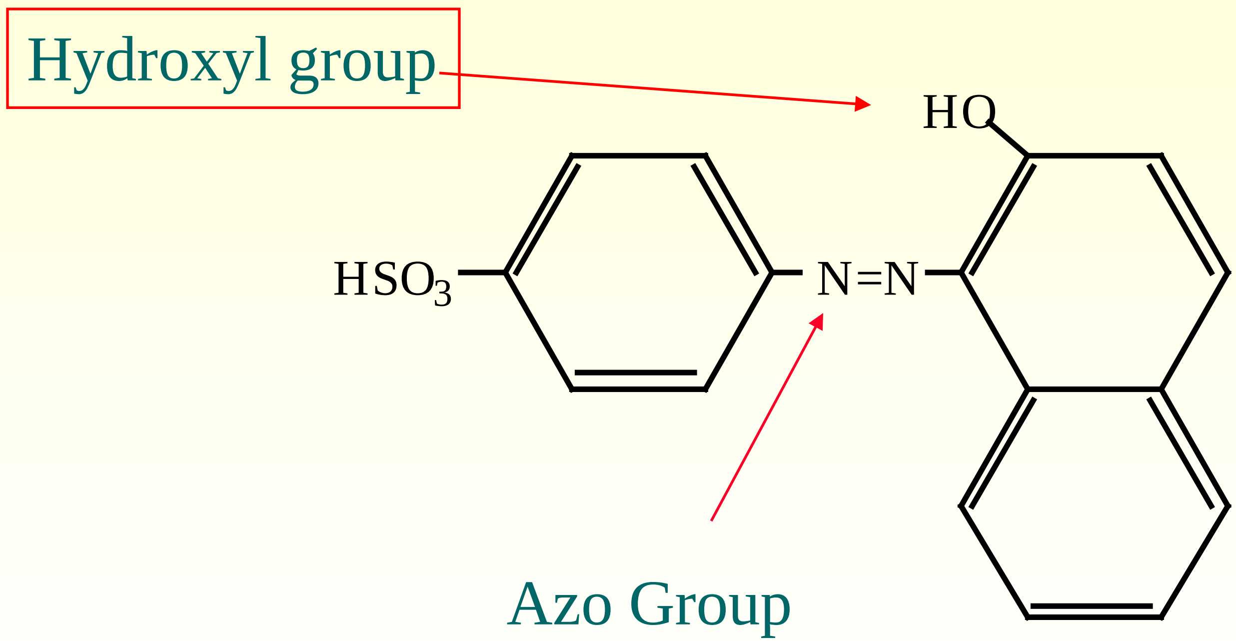
Azo group

- Brilliant colors ranging from reds to blues

  Methyl orange, Orange II, etc.

Orange II — a Diazo Dye

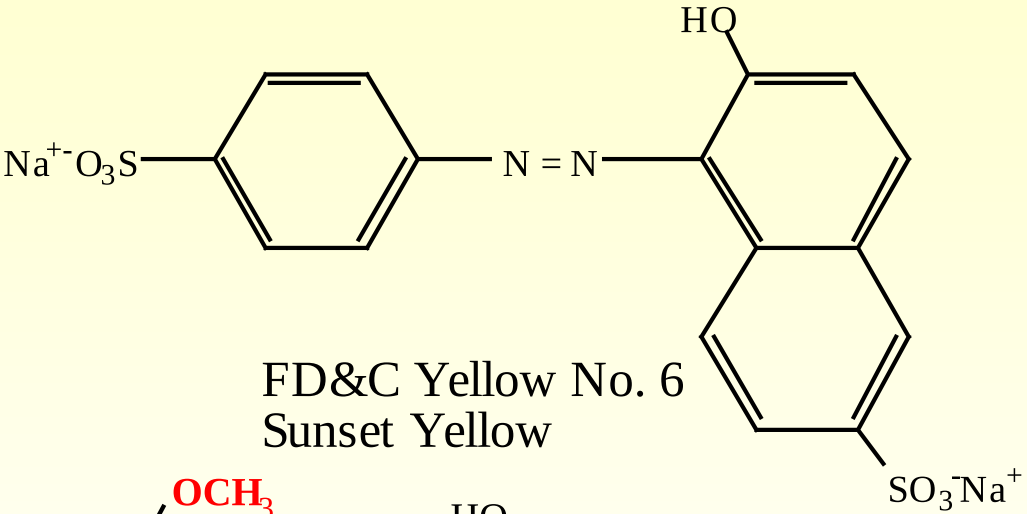
- The AZO group is the Chromophore



- The Hydroxyl group is an Auxochrome

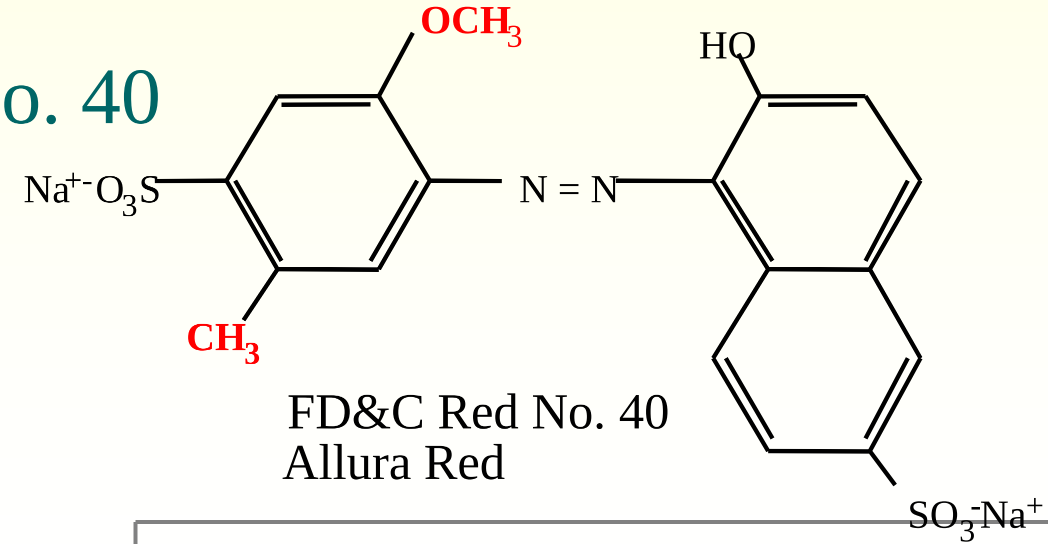
FD & C Food Colors

- Yellow No. 6



FD&C Yellow No. 6
Sunset Yellow

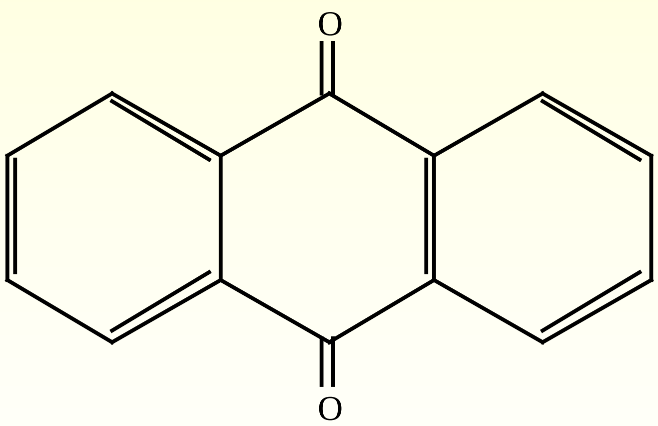
- Red No. 40



FD&C Red No. 40
Allura Red

CARBONYL Dyes

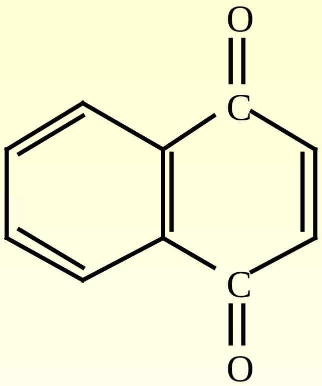
- Anthroquinone Dyes
  - Contain several —C =O groups
  - Multiple aromatic rings



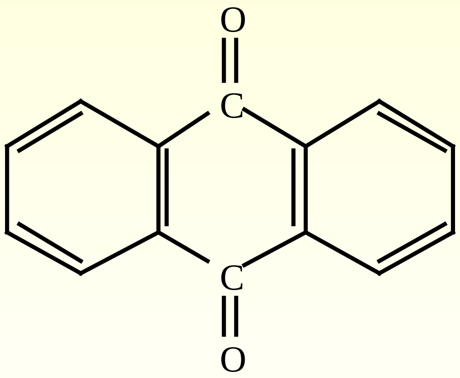
- Originate from plants
  - Coloring agents in flowers, fruits, vegetables

QUINOIDS

- Naphthaquinone



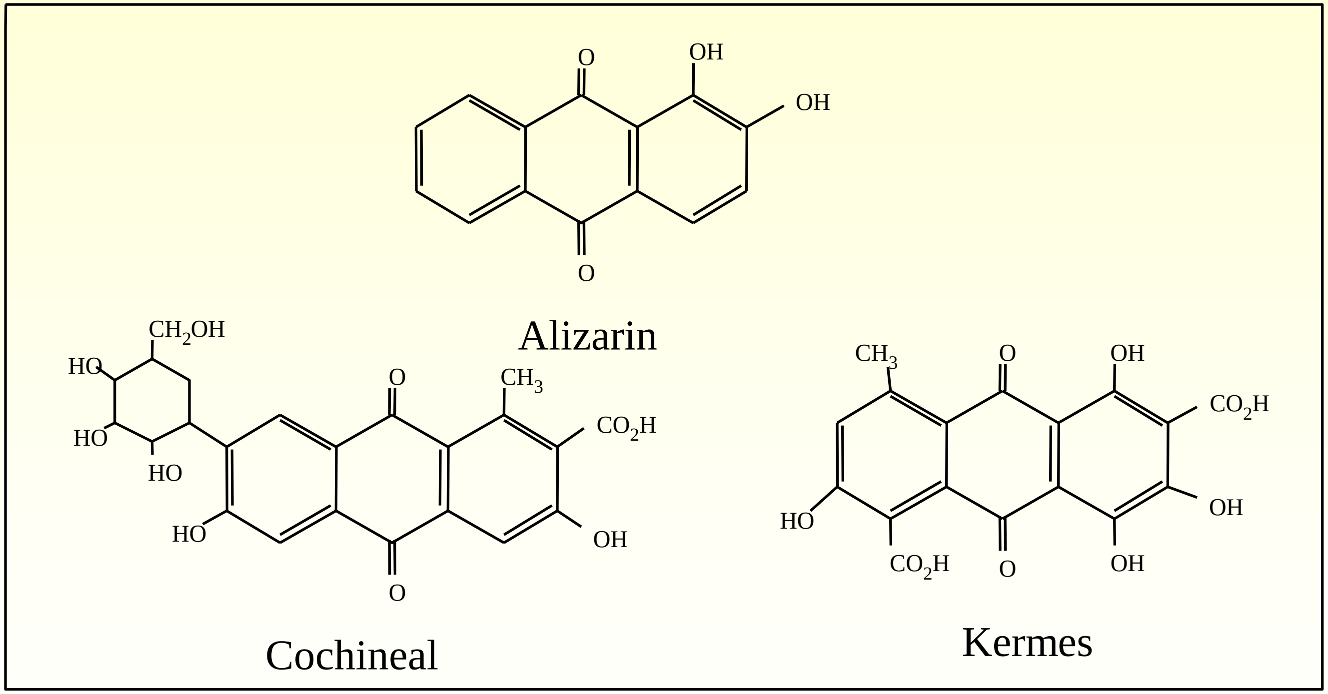
- Anthraquinone



- Red plant dyes and insect dyes
  - Alizarin, pupurin, rubiadin
  - Carminic acid, kermesic acid

Alizarin, Cochineal, Kermes

- All are carbonyl dyes — chromophores

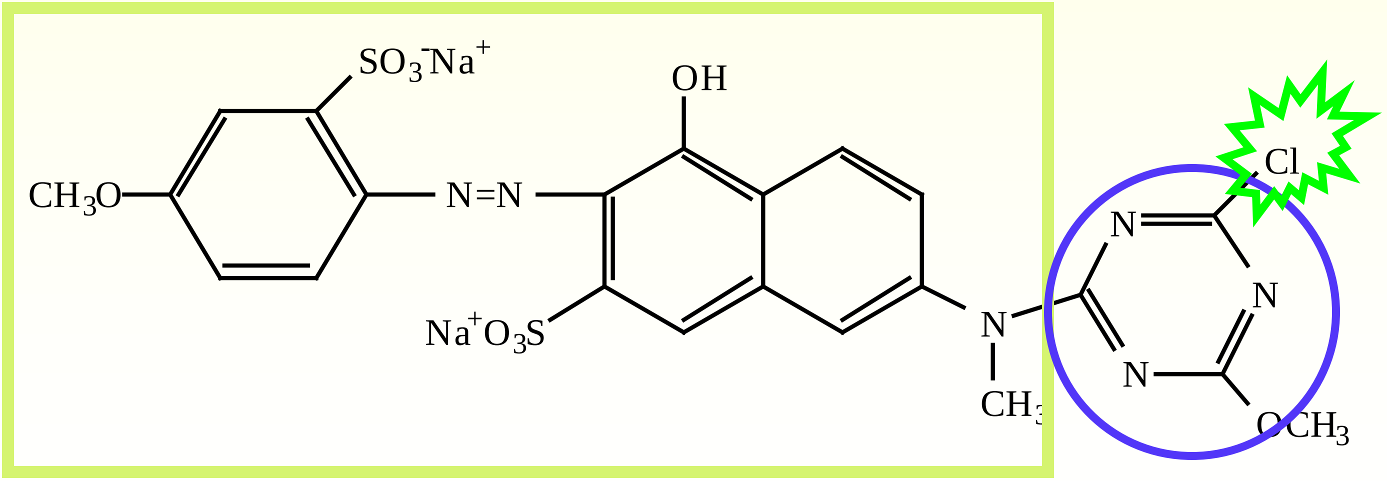


- Contain many Auxochrome groups

Fiber-Reactive Dye Structure

- **Chromophore**
- **Reactive group**
- **Leaving group**

Mono chlorotriazinyl dye



Procion Scarlet H-R, Cibacron Scarlet RP, Chlorine Reactive Red 3

Fastness in Dyes

- Stability of dyes towards light
- Dyes vary greatly in their lightfastness and colorfastness
- Undergo photo-oxidation and photo-reduction by light — dyes fade and degrade