Human History Through Fiber

How Fiber Changed the World

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Course Overview

- Week 1
  - Prehistory and early history
  - Process overviews of spinning and weaving
- Week 2
  - Hemp and flax and other bast fibers
  - Cotton
- Week 3: Silk
  - Silkworms and silk properties
  - Sericulture and silk in China
  - Silk Road and silk outside of China
- Week 4: Wooly mammals
- **Week 5**
  - **Dyeing**
  - **Synthetics**
  - **Contemporary fiber art**

Dye: a colored substance that chemically bonds to material to which it is applied

- Substantive dyes – bind directly to textile
- Mordant dyes – require chemical intermediary to bind to textile
  - Tannin – from tea leaves, oak galls, other plants
  - Alum – aluminum sulfate or potassium sulfate
    - Found in minerals, clays or evaporates
    - Used for dye in ancient times – at least back to 4000 BCE
    - Traded on Silk Roads
  - Iron – scrapings, or boil in iron pot – dulls or saddens colors

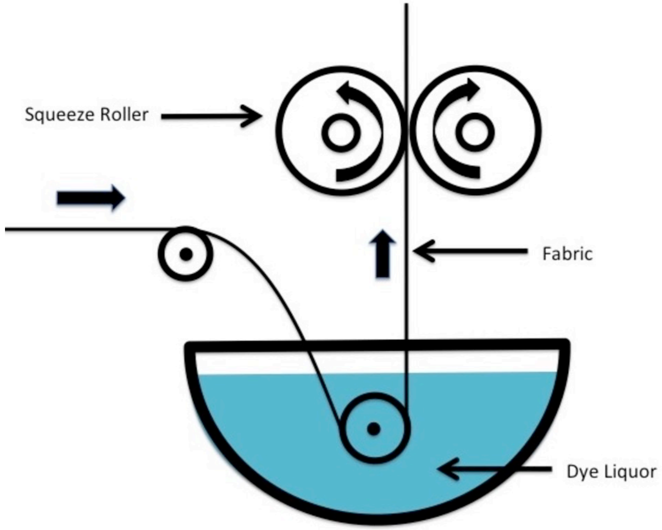
Dyeing Techniques

Dip

Kettle

Paint

Print



Resist Techniques

Batik

Ikat

Resist Techniques

Shibori

Tie dye

Natural colors - mineral

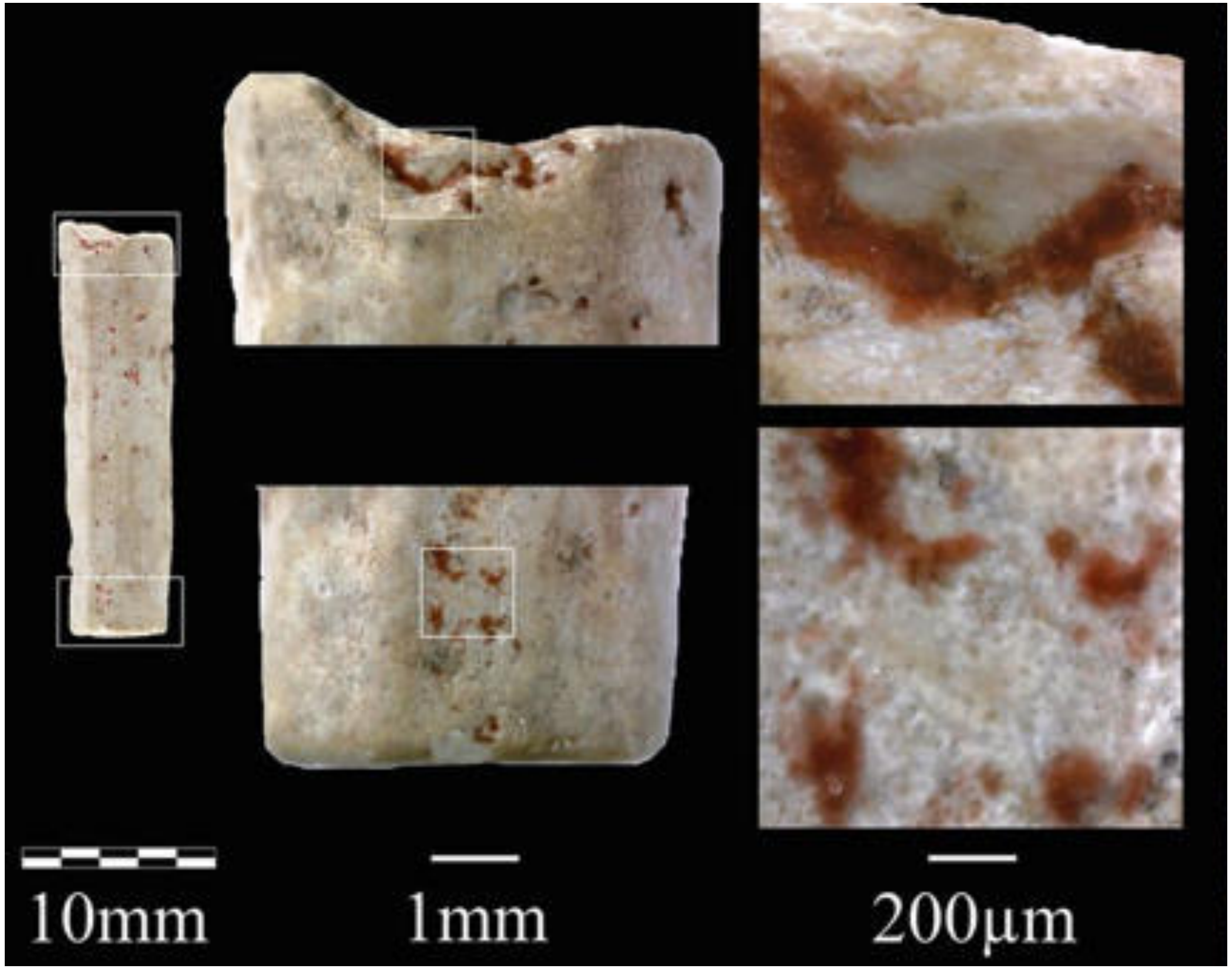
Ochre cave paintings going back 64,000 years

Maltravieso Caves
Spain 64,000 BP

Mali mud cloth

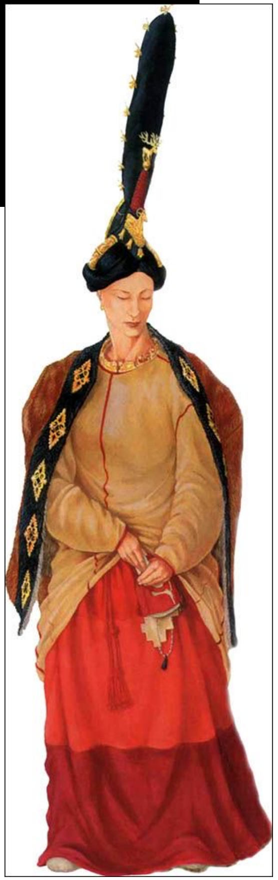
Natural Dyes - plant

Madder dyed beads 13,000 BCE Kebara cave in Israel



Natural dyes on fabric

- Dyed flax in Dzudzuana caves in Caucasus 36,000 yrs ago
- Indigo dyed cotton in Huaca Prieta Peru 6500 BCE
- Siberian Ice Maiden 5000 BCE – wool dyed with kermes
- Indigo and madder dyed linen in Egypt 2500 BCE
- Indigo, madder, murex dyed wool in Israel 1200 BCE

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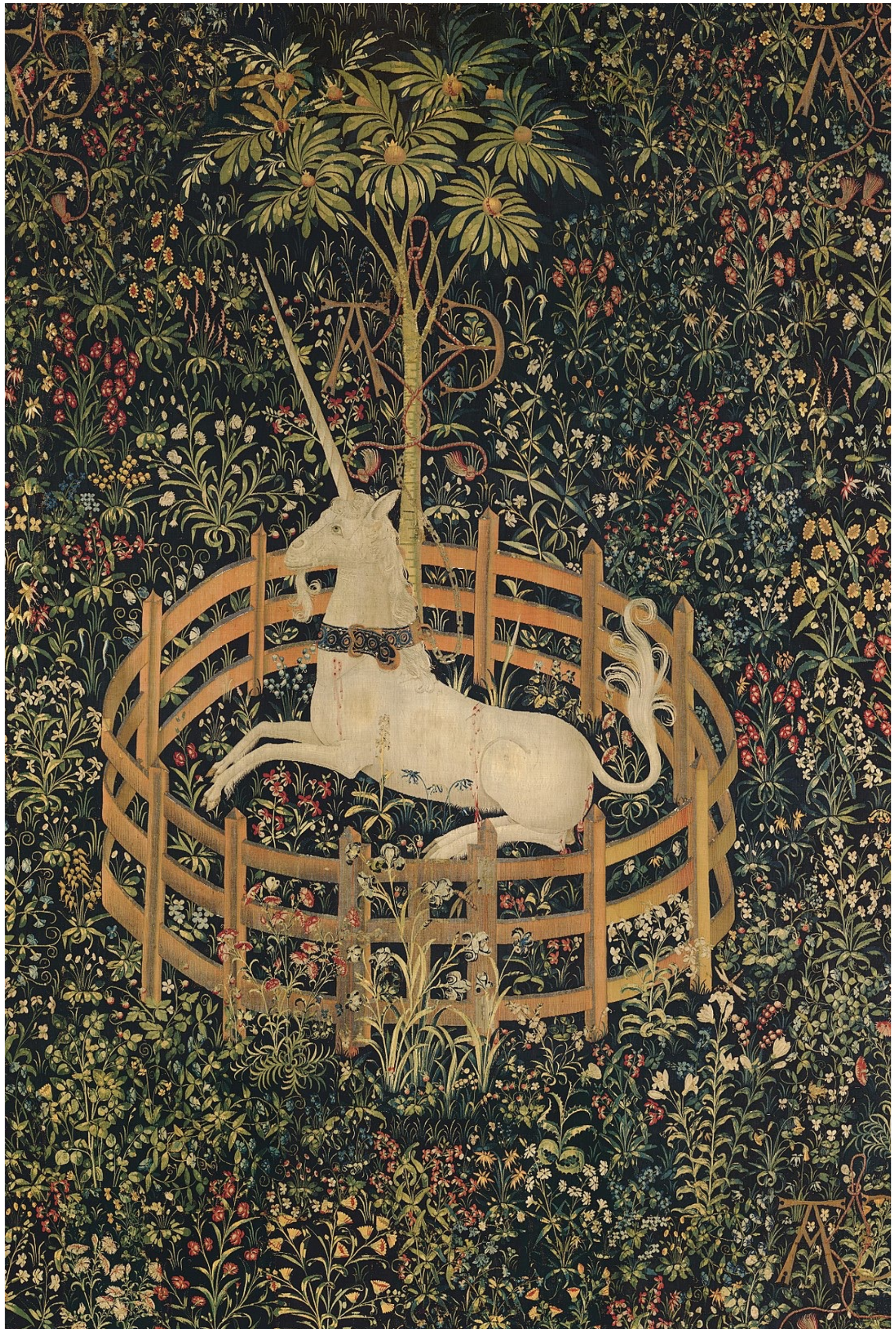
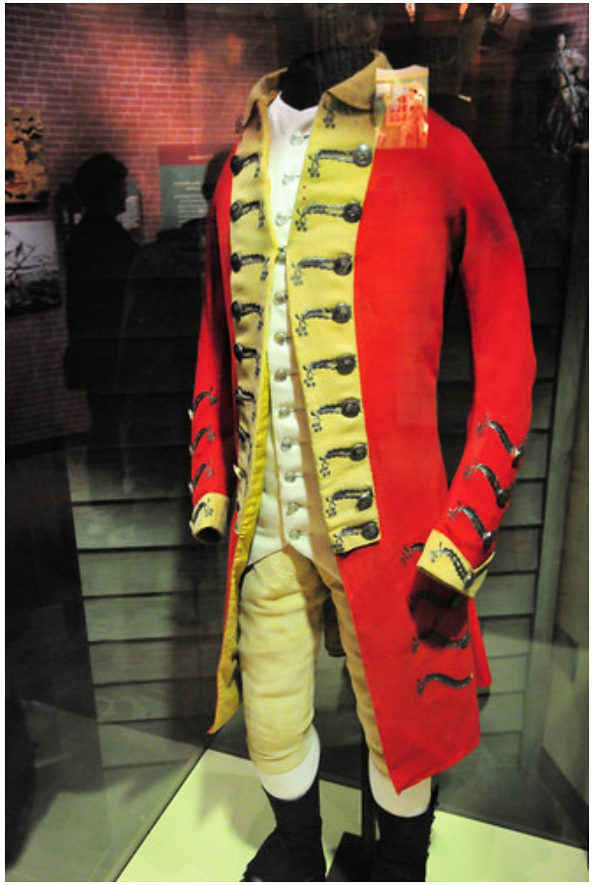


Weld
Reseda luteola

Madder

Rubia tinctorum




madder root
no mordant
alkaline modifier
madder root
alum mordant
madder root
iron mordant
alkaline modifier
Madder root
no mordant
alkaline modifier
cochineal overdye
alum mordant

Woad
Isatis tinctoria

[illegible]

Couleurs que la Cuve produit
Lorsqu'elle Est En etat de travail

La Cuve Estant assise avec quatre balles pastel Et 4 lt Indigo par balle, Rend les Couleurs cy apres.

4 Pces aile de Courbeau.
4 Pces bleu turquin.
4 Pces bleu de Roy
4 Pces bleu Celeste
4 Pces bleu d'azur.
4 Pces bleu de Ciel
4 Pces bleu mignon.
12 Pces bleu de blanchy de trois differentes nuances.

Il y a de plusieurs qualittes de bleus Compris dans les Reglemens generaux & particuliers, qui ne sont differents de Ceux cy que par leur degré de Couleur.

Woad

- Cultivated and exported as early as 1000 BCE in Britain
- Significant export commodity throughout medieval times
- Regulated with taxes and laws 1500's
  - England attempted to keep monopoly on export
- Church supported woad over indigo
  - called indigo color of the devil's eye and punished indigo dyers
- Queen Elizabeth I restricted amount of land for woad in 1586 due to famine from grain shortage
- Grown commercially in France, Germany, Flanders in medieval times but smaller part of economy compared with England.

  France regulated indigo:woad ratios
- Eventually replaced by indigo

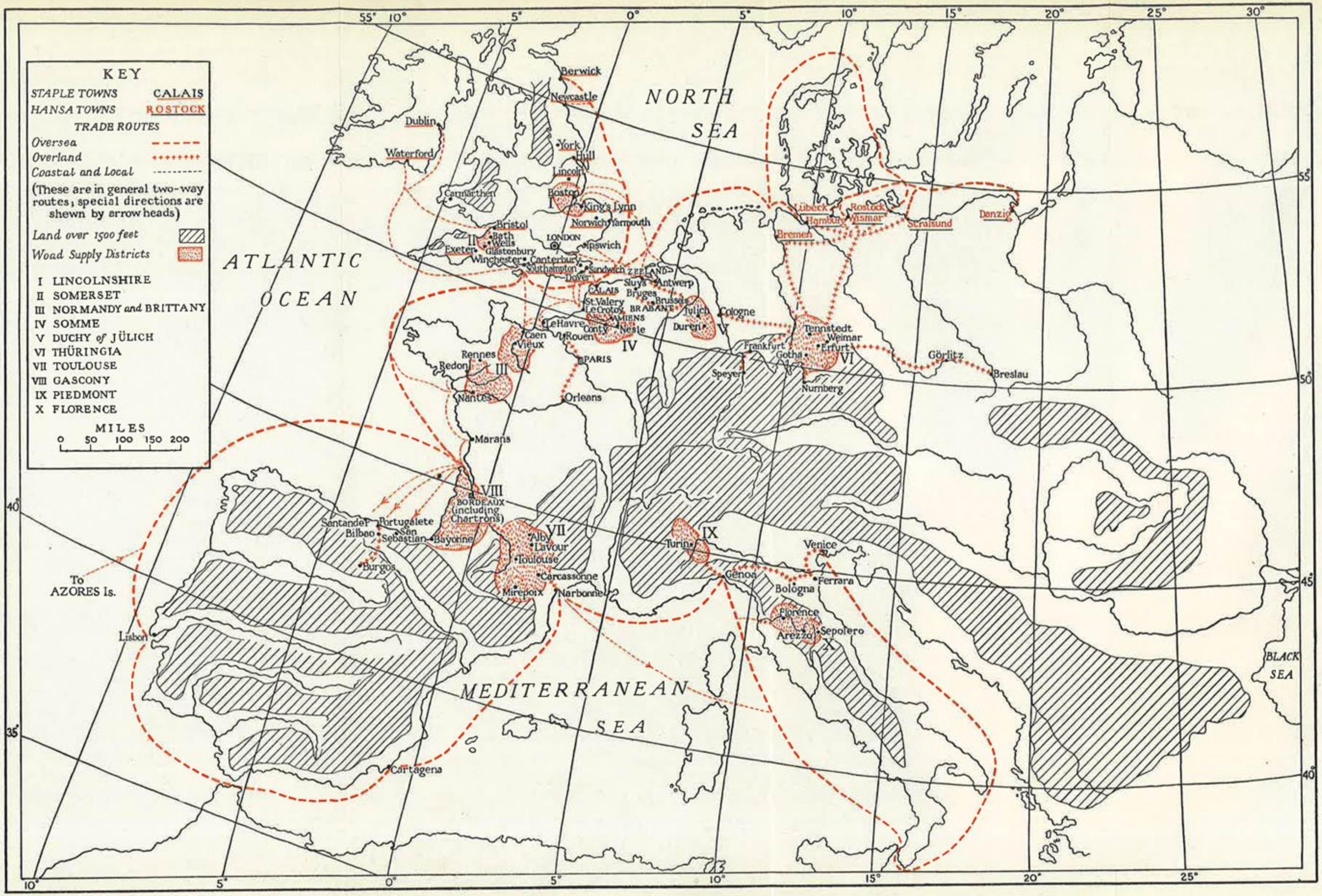
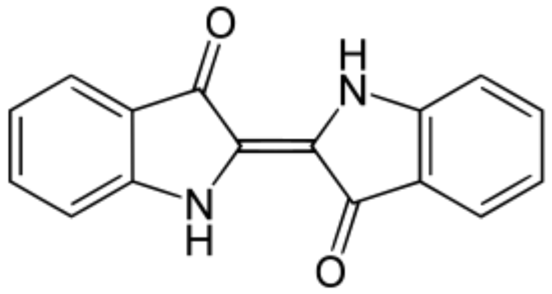


Fig. 11. MAP SHOWING THE TRADE-ROUTES OF WOAD AND THE CHIEF DISTRICTS OF PRODUCTION

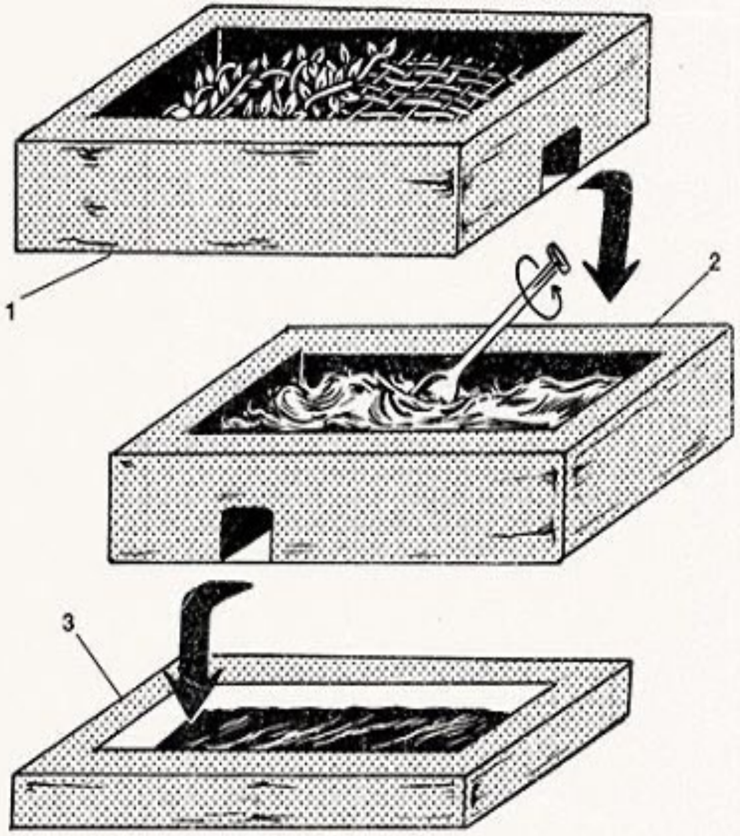
Indigo
Indigofera tinctora



PROCESS:

INDIGO DYE

Indigofera Tinctoria



1. Indigo leaves are harvested and placed in a fermentation vat.

2. Liquid is drained into 2nd vat and mixed with a paddle to allow oxidation.

3. Settled pigment is drained into a 3rd tank and heated to halt fermentation.


Boro3.3
3000ml

Indigo

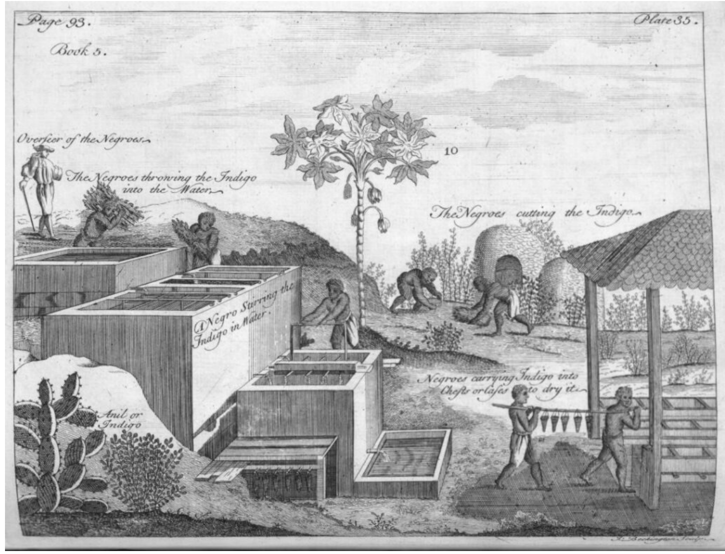
- Cultivated in Americas by 6500 BCE
- Cultivated in India, China, Mediterranean regions likely by around that time, but certainly by 4500 BCE
- Grown in Japan by 700, West Africa by 1200

Indigo as commodity

- Traded around the world at least from 3000 BCE
- Traded along Silk Roads
- Imported to Northern Europe from India, Egypt – first known 1140, London in 1276
- Imported to Spain from Americas with conquistadors 1500's
- Imported to Portugal from India 1500's
- In 17th Japan, farmers/dyers who gave away indigo secrets were beheaded

Indigo and Slavery

- Work intensive to grow, harvest and extract dye → inexorably linked to slavery
- European nations enslaved native peoples and West Africans in their Caribbean colonies to farm indigo (and cotton and sugarcane)
- South Carolina indigo industry 1739
  - Eliza Lucas Pinkney inherited her father’s plantation
  - When the price of rice dropped, she decided to grow indigo
  - Technical advisor was enslaved man from Monseratt
  - Began exporting in 1744, by 1748 exported 130,000 lb
  - One third of colonial pre-Revolutionary exports



Indigo and Slavery

British East India Co

- By late 1600's cultivated indigo for export using indentured native farmers – controlled by massive taxes on all other crops
- Indigo revolt 1859
  - Non-violent uprising of Bengali indigo farmers led by Gopal Modal resulted in violent clashes with British, trial and execution of some farmers
  - British commission appointed to study reasons for protest documented "extremely exploitive practices"

" not a chest of indigo reaches England without being stained by human blood"

End of Indigo Economy

- Adolf Baeyer first synthesized indigo pigment 1865

Murex *sp*
Bolinas bandaris

Murex - Tyrian purple

- Mucus secretion from gland in Murex spp, used to sedate its prey
- Can be “milked” from living snail, or recovered by crushing shells
- 12,000 snails needed for 1 gm dye – worth its weight in gold
- Possibly used by Minoans

Tyrian Purple production

Pliny the Elder d 79 AD

The most favourable season for taking these [shellfish] is after the rising of the Dog-star, or else before spring; for when they have once discharged their waxy secretion, their juices have no consistency: this, however, is a fact unknown in the dyers' workshops, although it is a point of primary importance. After it is taken, the vein [i.e. hypobranchial gland] is extracted, which we have previously spoken of, to which it is requisite to add salt, a sextarius [about 20 fl. oz.] to every hundred pounds of juice. It is sufficient to leave them to steep for a period of three days, and no more, for the fresher they are, the greater virtue there is in the liquor. It is then set to boil in vessels of tin [or lead], and every hundred amphorae ought to be boiled down to five hundred pounds of dye, by the application of a moderate heat; for which purpose the vessel is placed at the end of a long funnel, which communicates with the furnace; while thus boiling, the liquor is skimmed from time to time, and with it the flesh, which necessarily adheres to the veins. About the tenth day, generally, the whole contents of the cauldron are in a liquefied state, upon which a fleece, from which the grease has been cleansed, is plunged into it by way of making trial; but until such time as the colour is found to satisfy the wishes of those preparing it, the liquor is still kept on the boil. The tint that inclines to red is looked upon as inferior to that which is of a blackish hue. The wool is left to lie in soak for five hours, and then, after carding it, it is thrown in again, until it has fully imbibed the colour.

Tyrian Purple

- Commercialized by Phoenicians 1570 BCE
- Highly sought in Roman Empire – restricted to royalty - amount of purple worn signified rank
- Ptolemy beheaded allegedly because he wore purple to meet Roman emperor
- Possibly worn by King David

Bugs

Kermes

Cochineal

Tree Wood

Brazilwood

Logwood

Lichens and Mushrooms


Safflower
Cochineal
Brazilwood
Orange Cosmos
Red Cosmos
Coreopsis Roulette
Weld
Weld + Copper
Goldenrod
Chamisa
Indigo + Yarrow
Weld + Iron
Indigo
Indigo
Black Hollyhock
Logwood Extract
Logwood Bark

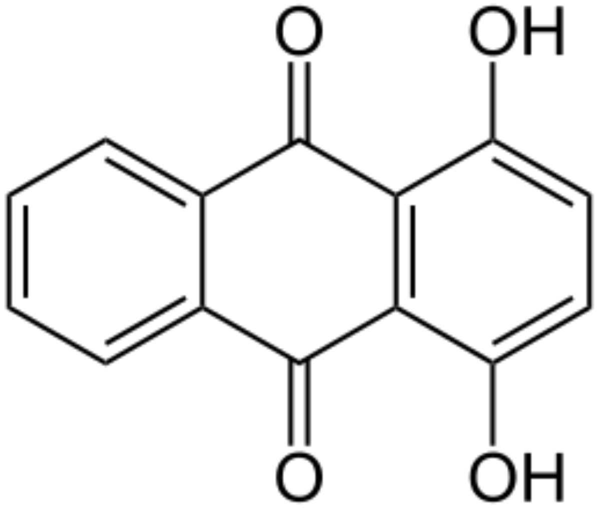
Comments and Questions

Some key aspects of natural dyes

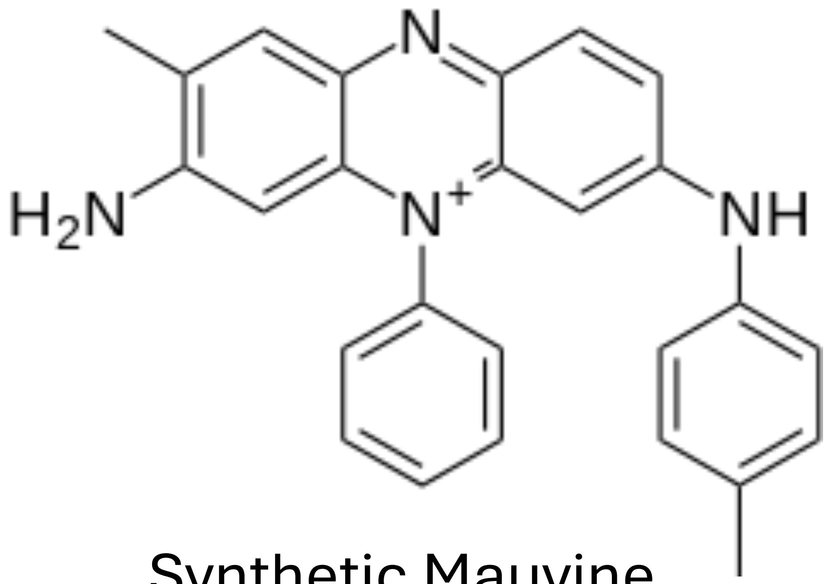
- All dyes up to the 1850's were natural, mostly from plant or animal sources
- Problems include:
  - Difficult and/or expensive to produce
  - Difficulty dyeing cellulose (linen, cotton, hemp, etc.)
  - Limited set of colors
  - Inadequate consistency
  - Inadequate color-fastness

A little chemistry

- Molecules are made from bonding atoms together
- Organic molecules contain carbon atoms
- Perceived color comes from absorption and scattering of light
- Specific wavelengths of light are absorbed by electrons in the molecules
- Electrons in certain organic rings tend to have the right energy levels to absorb light in the visible range



Alizarin from Madder



Synthetic Mauvine

A little more chemistry

- Most dyes do not form strong chemical bonds to the fibers; instead, they weakly attach based on chemical charges
- Cellulose fibers tend to have a waxy coat that is inaccessible to dyes dissolved in water
- After removing the waxy coat, cellulose fibers have only negatively charged groups, so bond best with positively charged dyes
- Protein fibers have both negative and positive charges, so are easier to dye with a wider variety of dyes
- **Mordants** act as a “bridge” between the fibers and the dyes
- Many characteristics of a dye bath affect dye and mordant binding including pH, water hardness, temperature, and dissolved ions

Triumphant story: Sir William Henry Perkin

- Discovered the first synthetic dye in 1856
- Joined the Royal College of Chemistry in London at age15 in 1854
- Chemists could deduce empirical formulas, but not structures
- His professor, AW Hofmann, asked him to try to synthesize quinine

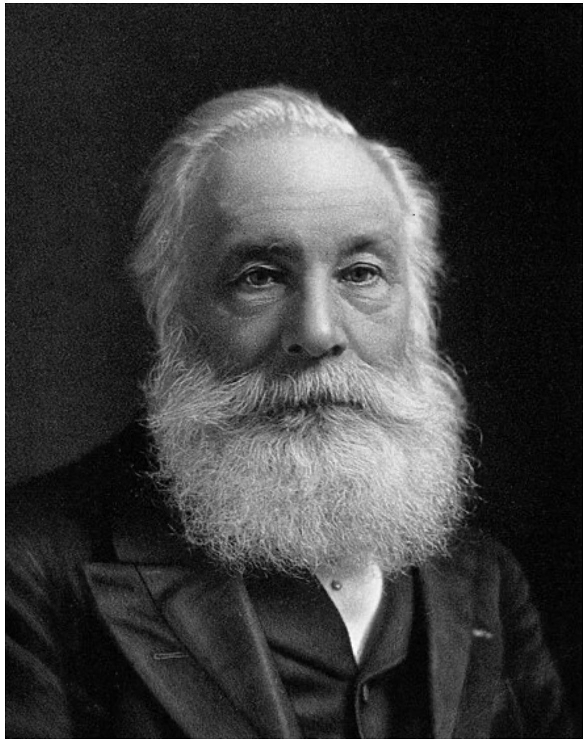
$$2(C_{10}H_{13}N) + 3\,O \xrightarrow{K_2Cr_2O_7,\ H_2SO_4} C_{20}H_{24}N_2O_2 + H_2O$$

Allyl toluidine — Quinine

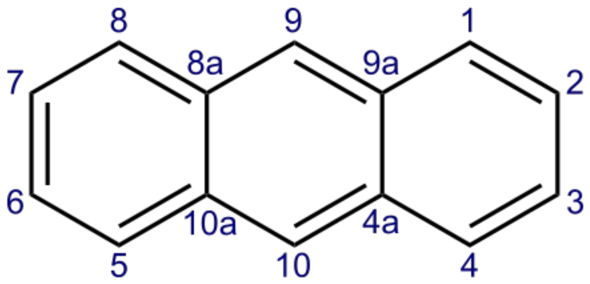
- He next tried aniline, another input derived from coal tars, and when he washed the product with methanol, a purple color resulted
- The dye was called aniline purple, mauve or mauvine
- He dyed some silk and sent it to a dye house and, when told it was good, applied for a patent

Sir William Henry Perkin, cont.

- Perkin left school, borrowed startup money from his father and went into manufacturing dyes at Perkin and Sons in 1857
- Within 25 years 90% of dyes were synthetic
- The structure of aniline purple was not identified until 1994!
- Perkin tried many variations and developed synthetic reds, pinks, violets and greens
- In 1865 BASF was founded in Germany and by 1872 was selling more dye than Perkin and Sons
- Perkin published more than 180 papers up to 1907, the year of his death
- His three sons all became chemists

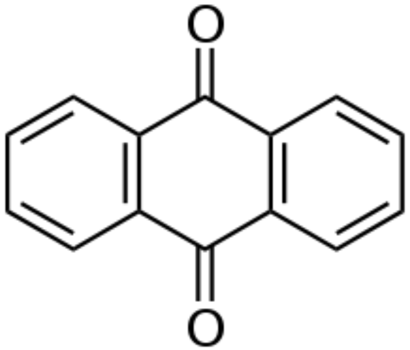


Coal tar example for synthetic dyes



Anthracene

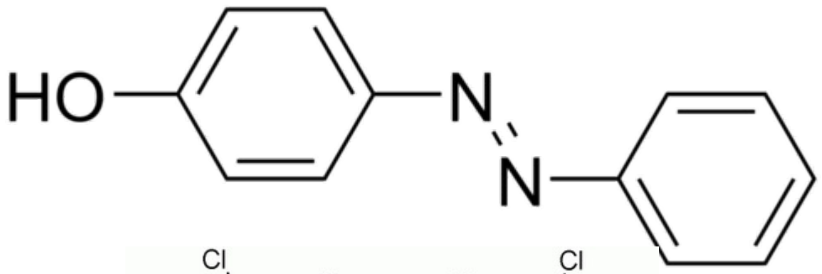
Anthraquinone



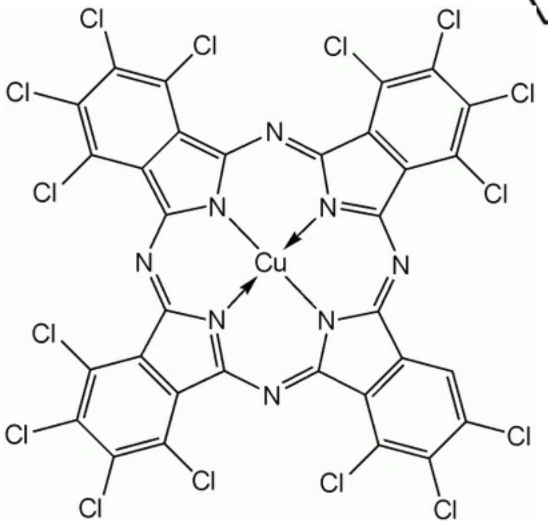
- Baking coal without oxygen produces coke, coal gas, and coal tar
- Anthracene, $C_{14}H_{10}$, makes up 1.5% of coal tar
- Adding oxygen gives anthraquinone
- (Modern synthesis of anthraquinone is by other means)
- Adding a variety of side groups to anthraquinone results in blue, violet and red dyes
- Natural anthraquinones include alizarin (madder), carminic acid (cochineal), and purpurin (Indian madder)

Other synthetic dye types

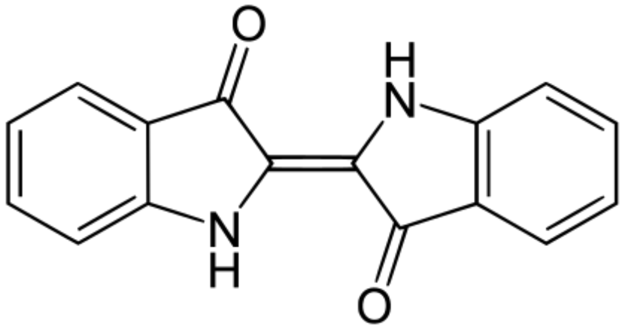
- Azo dyes are all synthetic; include red, yellow, blue and brown; and do not biodegrade



- Phthalocyanines have a complex ring structure; are blue to green; were discovered in the early 1900s; and are non-toxic



- Indigo is produced by the indigo plant, dyers knotweed or sea snails; is a blue dye; since around 1900 it is mostly produced synthetically



Commercial eco-dyeing

- Swisstex California is a major dyeing and finishing company in Los Angeles
- Since 1996 they have been incrementally improving their ecological footprint
- Clients include Nike, Adidas, and Under Armour
- 300,000 sq yards per day
- Exhaust gas goes to thermal oxidizer to break down hydrocarbons
- Captured steam is used to preheat the dye
- Typical water use is 25 to 75 gallons per pound of fabric; Swisstex went from 5 to 3 in the past decade

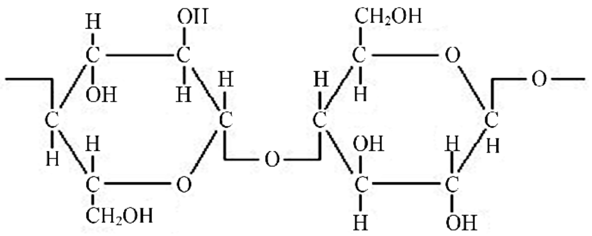
Synthetic dye summary

- Today 90% of fiber dyeing uses synthetic dyes
- They are cheaper and often easier to use
- Many have better colorfastness and consistency
- They produce a wider range of colors, especially bright ones
- Some are non-biodegradable
- Their manufacture may involve more pollution than natural dyes

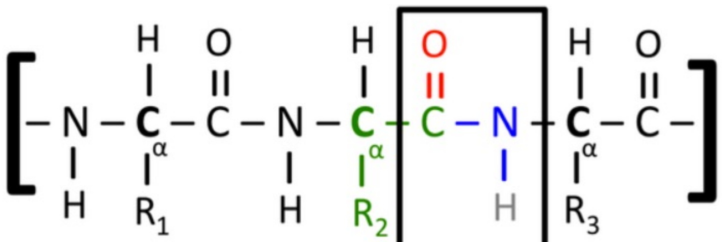
Polymer fibers chemical overview

- Almost all natural and synthetic fibers are polymers
- Polymers are chemically bonded chains made of simpler molecules

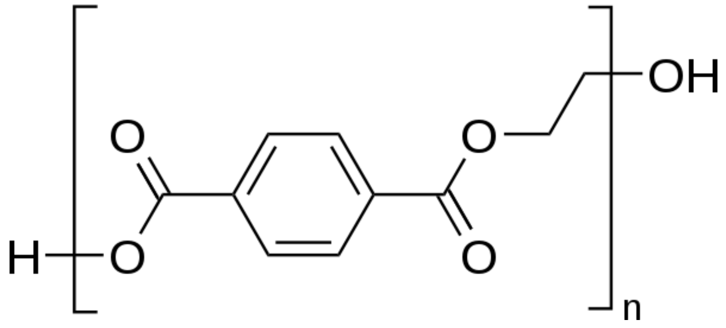
- Cellulose is a polymer of glucose



- Keratin and fibroin are proteins which are polymers of amino acids



- E.g., PETE is a polymer of ethylene-terephthalate (polyester Dacron™)



Rayon (Viscose)

- Rayon is a semi-synthetic fiber made by dissolving cellulose and extruding new fibers
- The source material is wood and agricultural scrap
- It has been commercially produced since 1905
- The most common solvent is alkaline carbon disulfide, a toxic liquid
- Lenzing AG produces Tencel™ using the more expensive, but less toxic process called “lyocell”, developed in North Carolina in 1972
- Can be made to resemble silk, wool, cotton or linen
- Dyes well and breathes well (good for hot and humid climates)
- Is biodegradable
- Accounts for about 23% of all synthetic fibers made

Sad story: Wallace Carothers

- Born in a small town outside of Des Moines, Iowa in 1896
- Completed the accountancy and secretarial curriculum at Capital City Commercial College in Des Moines in 1915
- Got a BS from Tarkio College in Missouri in 1920 and a PhD in chemistry from U. Illinois in 1924
- Instructor in chemistry at Harvard in 1926
- In 1927, DuPont tried to recruit him to head organic chemistry at their new pure research lab
- He refused, explaining that "I suffer from neurotic spells of diminished capacity which might constitute a much more serious handicap there than here.”
- A DuPont exec went to Harvard and convinced him; the salary was $500 a month vs. $267 at Harvard

Wallace Carothers at DuPont

- Carothers was in the minority who believed in the existence of macromolecules
- Interested in the new idea of polymerization, in 1930 he collaborated on the synthesis of Neoprene™ (MW ~26,000) from acetylene (MW 26)
- Also in 1930, his team produced the first silk-like polyester with a chain long enough (MW 12,000) for practical use
- Altogether he had 92 patents, all assigned to DuPont
- In 1934 he modified the polyester approach to make polyamides, which were stronger and more stable
- Later that year, he disappeared from work and was found in a psychiatric clinic
- Back to variations on polyamides, he made polyamide 6-6, Nylon™, with the formula $(C_{12}H_{22}N_2O_2)n$
- In 1936, two months after admission to the NAS, he was admitted to a psychiatric hospital, and he died by suicide with cyanide in 1937 at age 41

Nylon uses

- Nylon was first available commercially in 1938 as Dr. West's Miracle Tuft toothbrush
- At the 1939 World's Fair nylon stockings were introduced, and became a huge commercial success

Adeline Gray

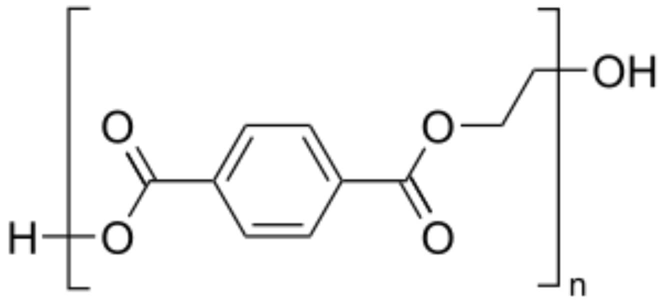
- Adeline Gray was a barnstorming pilot and parachutist and was the first to test a nylon parachute while working for DuPont in 1942
- The parachutes for the 1944 Normandy invasion were nylon

Acrylic (Orlon™)

- Nylon is marketed as a substitute for silk
- Acrylic, invented at DuPont in 1941, is marketed as a substitute for wool
- A polymer of acrylonitrile ($H_2C{=}CH{-}C{\equiv}N$)
- Among the least breathable fabrics, but is good for heat retention
- Much more flammable than wool
- Developed by DuPont but now mostly made in Asia
- Commonly used for sweaters, mittens, gloves, carpeting, upholstery and rugs

Polyester (Dacron)

- DuPont 1951
- ethylene terephthalate



- Marketed as a substitute for cotton
- Hypoallergenic, mildew-resistant, non-absorbent, and dries quickly, non-wrinkling

Easy-care and no-iron marketing

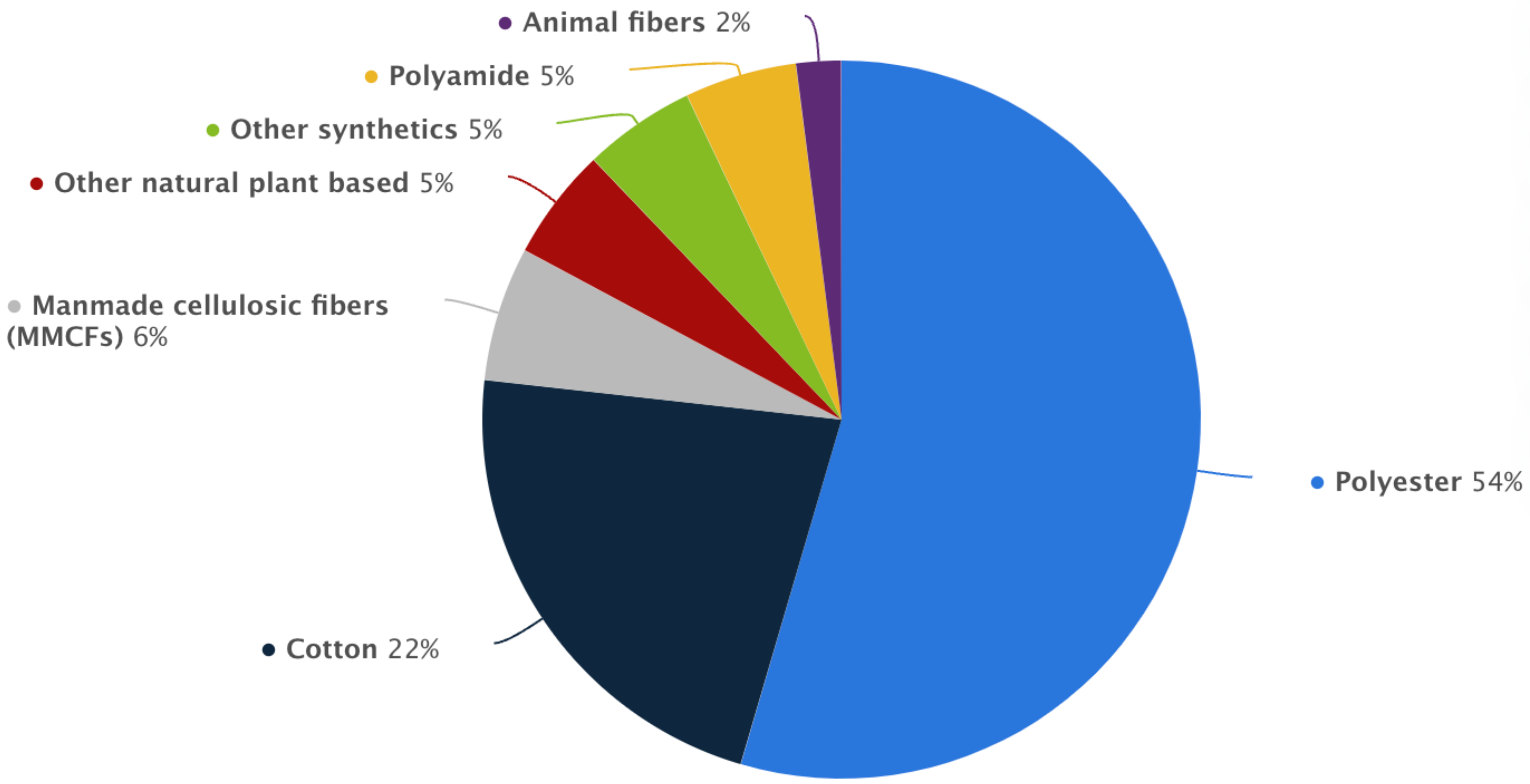
Kevlar

- A polymer related to Nylon, but with conjugated rings in the backbone
- Developed by Stephanie Kwolek at DuPont in 1965
- Strong enough for bullet-proof vests and spaceship parachutes
- Also used in tires, racing sails, drumheads, and mooring lines for ships
- A related fiber is flame-resistant Nomex, used in firefighting equipment and as electrical insulation

Microfiber

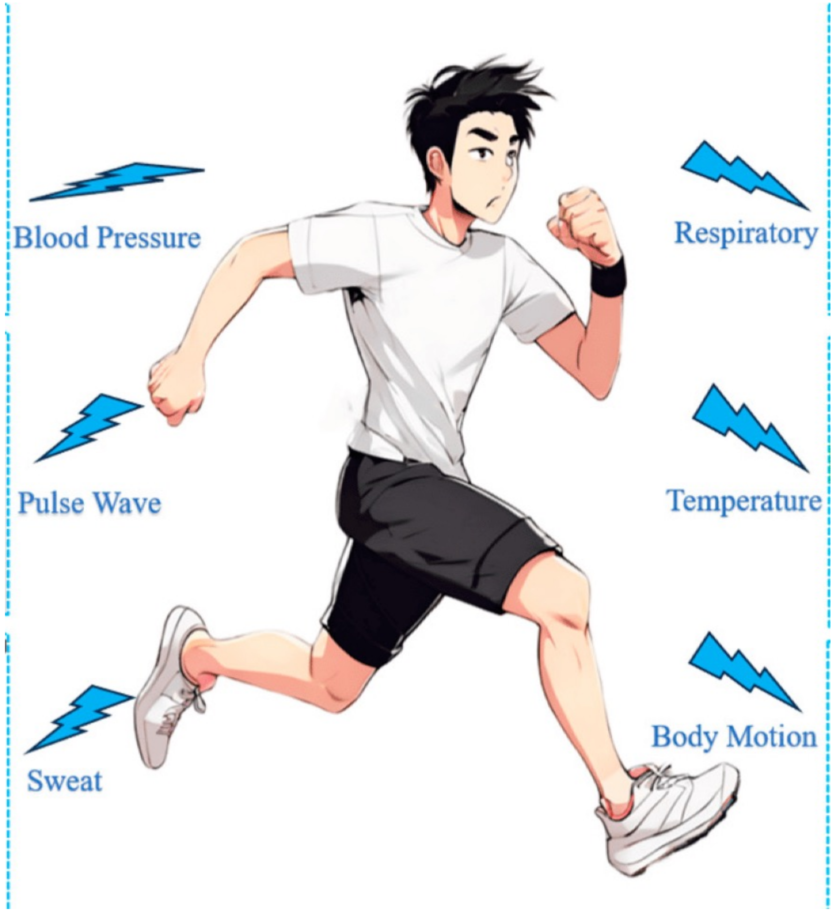
- Synthetic fibers can be extruded at smaller diameters to make microfiber
- It is soft, durable, water absorbent, and has electrostatic properties to make it a good filter for protective face masks
- Commercially successful starting in the 1990s, especially for washcloths, mopheads (e.g., Swiffer), kitchen towels, sheets and pillowcases
- Used in industrial filtration

Current breakdown of global textiles



Other high-tech fibers

- Spandex is a polyether, polyurea copolymer with high elasticity and strength
- NASA pioneered fabrics incorporating Phase Change Materials (PCM) to handle huge temperature extremes for space suits
- Cellulose or polyester fibers are added to asphalt to add strength and stability
- Steel structural cables are sometimes being replaced with Kevlar, carbon fibers, ultra-high-molecular-weight polyethylene (UHMWPE), and synthetic fiber composites
- “Smart” fabrics: Built in medical sensors, etc.



The brave new world of high-tech fabrics (1:54)

Synthetic fiber summary

- Synthetic fibers dominate the textile industry at 65%
- Benefits include cost and flexibility of manufacture
- They are generally not biodegradable, contribute to plastic pollution, and many need fossil fuel as feedstock

Comments and Questions

Yarn Bombing


UPMC


Sükufe


DZ 594MP


MARGARET UND CHRISTINE WERTHEIM
WERT UND WANDEL
DER KORALLEN

Yulia Ustinova



Ernesto Neto

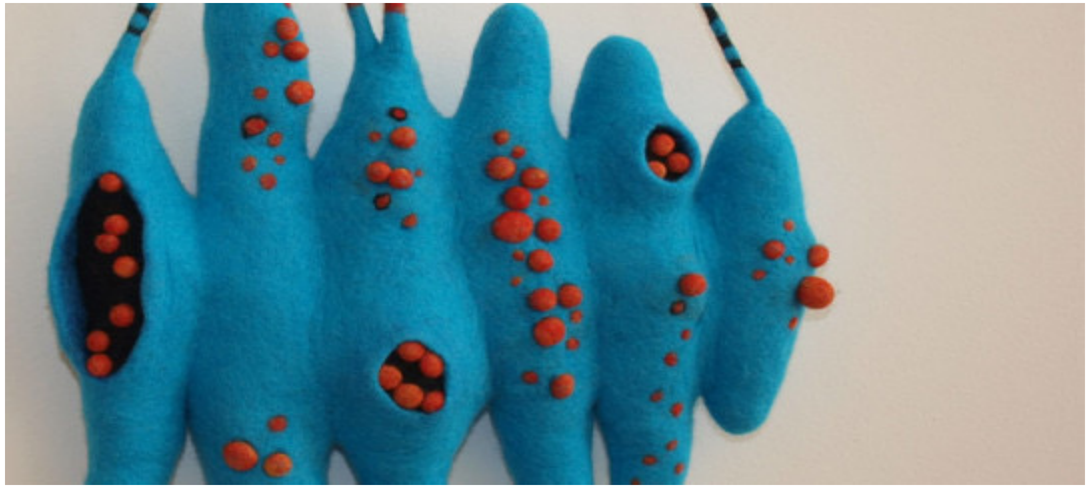
Sheila Hicks

Fiona Duthie

Ksenia Shinkovaskya

Dagmar Binder

Andrea Graham




Haliaeetus
leucocephalus


G12 Sandhill
Crane

Tim Harding

Gunta Stölzl (Bauhaus)

Sophie Standing

Comments and Questions

Thank you for your attention!