

Chapter 1 : chemistry of dyes

Azo dyes are organic compounds bearing the functional group $R-N=N-R'$, in which R and R' are usually calendrierdelascience.com are a commercially important family of azo compounds, i.e. compounds containing the linkage $C-N=N-C$. Azo dyes are widely used to treat textiles, leather articles, and some foods.

Natural dyes Until the 1800s virtually all dyes were obtained from natural sources, most commonly from vegetables, such as plants, trees, and lichens, with a few from insects. Solid evidence that dyeing methods are more than 4,000 years old has been provided by dyed fabrics found in Egyptian tombs. Ancient hieroglyphs describe extraction and application of natural dyes. Countless attempts have been made to extract dyes from brightly coloured plants and flowers; yet only a dozen or so natural dyes found widespread use. Undoubtedly most attempts failed because most natural dyes are not highly stable and occur as components of complex mixtures, the successful separation of which would be unlikely by the crude methods employed in ancient times. Nevertheless, studies of these dyes in the 19th century provided a base for development of synthetic dyes, which dominated the market by the late 19th century. The heterocyclic dye known as indigo is a naturally occurring compound that can be obtained from plants in the genus *Indigofera*. Two natural dyes, alizarin and indigo, have major significance. Alizarin is a red dye extracted from the roots of the madder plant, *Rubia tinctorum*. Two other red dyes were obtained from scale insects. These include kermes, obtained from *Coccus ilicis* or *Kermes ilicis*, which infects the Kermes oak, and cochineal, obtained from *Dactylopius coccus*, which lives on prickly pear cactus in Mexico. The principal coloured components in these dyes are kermesic and carminic acids, respectively, whose similarity was established by the 19th century. In their natural state many colorants are rendered water-soluble through the presence of sugar residues. These sugars, however, are often lost during dye isolation procedures. Probably the oldest known dye is the blue dye indigo, obtained in Europe from the leaves of the dyerswoad herb, *Isatis tinctoria*, and in Asia from the indigo plant, *Indigofera tinctoria*. Even by modern standards, both alizarin and indigo have very good dyeing properties, and indigo remains a favoured dye for denim, although synthetic indigo has replaced the natural material. Dyerswoad, *Isatis tinctoria*, is a source of indigo, considered the oldest known dye. With a process developed by the Phoenicians, a derivative of indigo, Tyrian purple, was extracted in very small amounts from the glands of a snail, *Murex brandaris*, indigenous to the Mediterranean Sea. Experiments in the 19th century yielded 1. Historically, this dye was also called royal purple because kings, emperors, and high priests had the exclusive right to wear garments dyed with it, as is well documented in the Hebrew Bible and illustrated for Roman emperors on mosaics in Ravenna, Italy. By the 19th century, with the decline of the Eastern Roman Empire, the Mediterranean purple industry died out. Natural yellow dyes include lutein, from the leaves of weld, *Reseda luteola*, and quercetin, from the bark of the North American oak tree, *Quercus tinctoria*. These are in the flavonoid family, a group of compounds occurring almost exclusively in higher plants and producing the colours of many flowers. In fact, these compounds can produce all the colours of the rainbow except green. Luteolin, a yellow crystalline pigment, was used with indigo to produce Lincoln green, the colour associated with Robin Hood and his merry men. Another group of compounds, the carotenoids, present in all green plants, produce yellow to red shades. Lycopene, from which all carotenoids are derived, produces the red colour of tomatoes. An ancient natural yellow dye, crocetin, was obtained from the stigmas of *Crocus sativus*; this dye is undoubtedly derived from lycopene in the plant. Few of the flavonoid and carotenoid colorants would have survived ancient extraction processes. Logwood is the only natural dye used today. Heartwood extracts of the logwood tree, *Haematoxylon campechianum*, yield haematoxylin, which oxidizes to haematein during isolation. The latter is red but in combination with chromium gives shades of charcoal, gray, and black; it is used mainly to dye silk and leather. Mordants Highly skilled craftsmen with closely guarded secret formulas rendered dyeing a well-protected trade. The formation of different colours by mixing red, blue, and yellow dyes was well known in ancient times, as was the use of metal salts to aid the retention of dyes on the desired material and to vary the resultant colours. These are adsorbed on the fibre and react with the dye to produce a less soluble form that is held to the fabric. No doubt the secret processes included other ingredients to improve the final results. Mordants also were used to vary the colours produced

from a single dye. For example, treatment with aluminum hydroxide, Al OH_3 , before dyeing with alizarin produces Turkey red, the traditional red of British and French army uniforms. Alizarin gives violet colours with magnesium mordants, purple-red with calcium mordants, blue with barium mordants, and black-violet with ferrous salts. Around 1850, chromium salts, used as mordants, were found to provide superior dye retention and, in time, largely displaced the others; chromium mordants are still widely used for wool and, to some extent, for silk and nylon.

Decline of natural dyes Until the dye industry utilized natural dyes almost exclusively; however, by nearly 90 percent of industrial dyes were synthetic. Several factors contributed to the commercial decline of natural dyes. By the Industrial Revolution in Europe led to a burgeoning textile industry, which created increased demand for readily available, inexpensive, and easily applied dyes and revealed the important economic limitations of natural dyes. Since most dyes were imported from distant sources, transportation delays were likely to slow the production of dyed materials. In addition, inefficient processes were often required for optimum results; for example, Turkey red dyeing could involve more than 20 steps to produce the desired bright, fast colour. Advances in organic chemistry, both practical and theoretical, spurred by studies of the many new compounds found in coal tar, increased interest in finding ways to utilize this by-product of coke production. The dye industry played a major role in the development of structural organic chemistry, which in turn provided a sound scientific foundation for the dye industry.

Synthetic dyes In the first commercially successful synthetic dye, mauve, was serendipitously discovered by British chemist William H. Perkin, who recognized and quickly exploited its commercial significance. The introduction of mauve in triggered the decline in the dominance of natural dyes in world markets. Mauve had a short commercial lifetime lasting about seven years, but its success catalyzed activities that quickly led to the discovery of better dyes. Today only one natural dye, logwood, is used commercially, to a small degree, to dye silk, leather, and nylon black. Some early commercial synthetic dyes. The synthetic dye industry arose directly from studies of coal tar. By coal tar was an industrial nuisance because only a fraction was utilized as wood preservative, road binder, and a source of the solvent naphtha. Fortunately, it attracted the attention of chemists as a source of new organic compounds, isolable by distillation. A leading researcher in this area, German chemist August Wilhelm von Hofmann, had been attracted to England in to direct the Royal College of Chemistry. In the following 20 years, he trained most of the chemists in the English dye industry, one of whom was Perkin, the discoverer of mauve. The success of mauve led to demands by English textile manufacturers for other new dyes. By trial and error, reactions of coal tar compounds were found to yield useful dyes. However, Hofmann became disenchanted with this purely empirical approach, insisting that it was more important to understand the chemistry than to proceed blindly. In he returned to Germany, and by most of his students had been lured to German industrial positions. By more than 50 compounds had been isolated from coal tar, many of which were used in the developing German chemical industry. Advances in the understanding of chemical structure, combined with strong industrial-academic interactions and favourable governmental practices, gave a setting well-suited for systematic development based on solid scientific foundations. Only a few Swiss firms and one in England survived the strong competition generated by the vigorous activity in the German dye industry. Recognition of the tetravalency of carbon and the nature of the benzene ring were key factors required to deduce the molecular structures of the well-known natural dyes e. These structural questions were resolved, and industrial processes based on chemical principles were developed by the beginning of the 20th century. There was also interest in the effects of dyes on living tissue. In the Danish microbiologist Hans Christian Gram discovered that crystal violet irreversibly stains certain bacteria but can be washed from others. The dye has been widely used ever since for the Gram stain technique, which identifies bacteria as gram-positive the stain is retained or gram-negative the stain is washed away. The German medical scientist Paul Ehrlich found that methylene blue stains living nerve cells but not adjacent tissue. He proposed that compounds may exist that kill specific disease organisms by bonding to them without damaging the host cells and suggested the name chemotherapy the treatment of diseases by chemical compounds. Gram-negative bacilli, *Klebsiella pneumoniae*, isolated from a lung abscess in a patient with pneumonia. Gram-positive cocci, *Staphylococcus aureus*, in a laboratory culture. Other uses were explored for compounds discovered during coal tar research; examples include aspirin an analgesic and saccharin a

sweetener. Coal tar studies became the foundation of the synthetic chemical industry, because coal tar was the major source of raw materials. However, coal by-products became less popular with the emergence of petroleum feedstocks in the 19th century, which gave rise to the petrochemical industry. The British government was forced to aid rejuvenation of its own dye industry; one measure brought several companies together, later to become part of Imperial Chemical Industries ICI, modeled after the Bayer and BASF combines in Germany. In the United States a strong coal tar chemical industry quickly developed. After the war, leadership in organic chemistry began to shift from Germany to Switzerland, Britain, and the United States. In contrast to the combines of Europe, independent firms developed in the U.S. A few new dye types were introduced in the 20th century, and major challenges were posed by the introduction of synthetic fibres, which held a major share of the world market, and by technological advances. Dye structure and colour Advances in structural theory led to investigations of correlations between chemical constitution and colour. In Germany chemists Carl Graebe and Carl Liebermann recognized that dyes contain sequences of conjugated double bonds: In Germany chemist Otto Witt proposed that dyes contained conjugated systems of benzene rings bearing simple unsaturated groups. These ideas remain valid, although they have been broadened by better recognition of the role of specific structural features. He had also claimed that auxochromes impart dyeing properties to these compounds, but it later became clear that colour and dyeing properties are not directly related. Witt suggested the term chromogen for specific chromophore-auxochrome combinations. The visible spectrum, which represents the portion of the electromagnetic spectrum that is visible to the human eye, absorbs wavelengths of 400–700 nm. Examples of dyes, each containing a different chromophore, include azobenzene, xanthene, and triphenylmethane. Alizarin contains the anthraquinone chromophore. These four dyes were commercial products in the late 19th century. The colours of dyes and pigments are due to the absorption of visible light by the compounds. The electromagnetic spectrum spans a wavelength range of metres, from long radio waves about 10 km [6]. Organic compounds absorb electromagnetic energy, but only those with several conjugated double bonds appear coloured by the absorption of visible light see spectroscopy: Without substituents, chromophores do not absorb visible light, but the auxochromes shift the absorption of these chromogens into the visible region. In effect, the auxochromes extend the conjugated system. Absorption spectra plots of absorption intensity versus wavelength are used to characterize specific compounds. In visible spectra, the absorption patterns tend to be broad bands with maxima at longer wavelengths corresponding to more extended conjugation.

Chapter 2 : Brief History of Dyes - Assignment Point

azo dyes, as well as the reaction conditions, and the new process was now taken up by all the leading dye firms. In Germany, this encouraged moves towards a unified patent law, which was introduced in

Druding Originally written for a Seminar presented in Seattle, Washington at Convergence , a bi-annual gathering of weavers, dyers and spinners BC Earliest written record of the use of dyestuffs in China BC Wool dyeing established as craft in Rome BC Alexander finds year old purple robes when he conquers Susa, the Persian capital. It is a Greek work. It cost its weight in gold. Late 4TH Century Emperor Theodosium of Byzantium issued a decree forbidding the use of certain shades of purple except by the Imperial family on pain of death AD Murex the mollusk from which purpura comes becoming scarce due to huge demand and over harvesting for Romans. A directory of weavers and spinners was published as well. The 3 major dyes were now: This became the first luxury dye of the Middle Ages just as Imperial Purple Murex had been for the ancient world. They send back brightly printed fabrics showing that the Indians knew about block printing prior to the Conquest. Cochineal from Mexico and Peru now being shipped back to Spain. At first they thought the fabric was linen, not cotton. This contract continued into the 20th Century still using cochineal. Prussian blue formed from prussite of potash and iron salt copperas. Actually one of the early chemical dyes. One of only 2 natural dyes whose discoverer is known, it yields a yellow, brighter than fustic, and is from the inner bark of No. Other oxidizing agents began to be used, too: This began the famous Toiles de Jouy production. It consisted of a wax or other resist on the background, actually a batik technique done on large scale. This helped to pave the way to the development of aniline basic dyes 22 years later. The process was called "mercerization". It was a brilliant fuchsia type color, but faded easily so our idea of the color mauve is not what the appearance of the original color was. Perkin also synthesized it about the same time, but independently. It was not marketed until Thomas and Holliday, England, synthesized the first azo dye formed on the fabric by coupling. Vacanceine red formed by treating fabric with naphthol and then dipping in a diazotized amine, a very fast category of dyes. B naphthol and nitraniline Chardonnet, France, made the first successful rayon and showed it at the Paris Exposition of This is now the most common process for manufacture of rayon. All aniline dyes were seized and publicly burned. Penalties included jail and fines equal to double the value of the merchandise. The average consumer consumption per capita of fibers: Carolina would begin to manufacture Dacron polyester. Druding for her dye seminar at Convergence They are not to be reproduced without permission, please. Druding Note from Susan: Normally, I would have a bibliography or list of references attached to this sort of historical listing, but since I wrote this for a lecture given more than 14 years ago I was lucky to have even found the copy of the list, much less my sources. I would be pleased to hear from anyone with corrections, additions or suggestions for updating this list, but I am unable to supply any additional information specifically for this list. For some bibliography on dye chemistry and history see the special TAN reprint on fiber reactive dyes here. Susan Also visit Index of Articles at Equilters.

Chapter 3 : History of Dyes from BC to 20th Century - natural dyes, synthetic

Tartrazine is a yellow acid azo dye discovered in and still in common use. Other azo dyes contain chemical groups that bind metal ions. Among numerous metal salts used with these dyes, chromium and copper are most common; often, the metal ion also unites with the fibre, improving the resistance of the dye to washing.

Fibers[edit] In the laboratory, home, or art studio, the acid used in the dye-bath is often vinegar acetic acid or citric acid. The uptake rate of the dye is controlled with the use of sodium chloride. In textiles , acid dyes are effective on protein fibers, i. They are also effective on silk. Medical[edit] In staining during microscopic examination for diagnosis or research, acid dyes are used to color basic tissue proteins. In contrast, basic dyes are used to stain cell nuclei and some other acidic components of tissues. The classes overlap and generally depend on type of fiber to be colored as well as the process used. They are normally sold as the Sodium salt , therefore they are in solution anionic. Animal protein fibers and synthetic nylon fibers contain many cationic sites. Therefore, there is an attraction of anionic dye molecule to a cationic site on the fiber. The strength fastness of this bond is related to the tendency of the dye to remain dissolved in water over fixation to the fiber. Structures[edit] The chemistry of acid dyes is complex and diverse. Most acid dyes are related in basic structure to the following: Many acid dyes are synthesized from chemical intermediates that form anthraquinone-like structures as their final state. Many blue dyes have this structure as their basic shape. The structure predominates in the leveling class of acid dye. Most azo dyes are not acid dyes, but many acid dyes are azo dyes. Many acid dyes of the azo type are red in color. These predominate in the milling class of dye. There are many yellow and green dyes commercially applied to fibers that are related to triphenylmethane. Classes of acid dyes[edit] Three typical classification of acid dyes are: These dyes are of relatively low molecular weight, thus they migrate rapidly before fixation. Associated with their high mobility, leveling dyes exhibit low wet fastness therefore normally not suited for apparel fabric. These dyes are applied at low pH, often using sulfuric acid and sodium sulfate mixtures. These dyes are of relatively high molecular weight, thus they migrate more slowly than leveling dyes. Associated with their low mobility, milling dyes exhibit better wet fastness than leveling dyes. These dyes are applied at higher pH, often using acetic acid. Metal complex acid dyes: More recent chemistry combined transition metals with dye precursors to produce metal complex acid dyes with the highest light fastness and wet fastness. These dyes are also very economical. They produce, however, duller shades.

Chapter 4 : Acid dye - Wikipedia

The simplest azo dyes are yellow, but changing the number of chromophores or the backbone structure can produce red, violet, blue and even black dyes. Azo dyes are used as textile colorants, and well as in industrial paints, printing inks, varnishes, plastics, crayons and other products.

Term Paper Brief history of dyes The uses of colorants by mankind for painting and dyeing of their surroundings, their skins and their cloths dates back to the dawn of civilization. Until the middle of the 19th century, all colorants applied were from natural origin. For example, inorganic pigments such as soot, manganese oxide, hematite and ochre have been utilized within living memory; organic natural colorants have also a timeless history of application, especially as textile dye. These dyes are all aromatic compounds, originating from plants but also from insects, fungi and lichens. Synthetic dye manufacturing started in , when the English chemist W. Perkin in an attempt to synthesize quinine, obtained instead a bluish substance with excellent dyeing properties that latter known as aniline purple, Tyrian purple or mauveine. Perkin patented his invention and set up a production line. In the beginning of the 20th century, synthetic dyestuffs had almost completely supplanted natural dyes. Dyes contain chromophores, delocalized electron systems with conjugated double bonds, and auxochromes, electron withdrawing or electron donating substituents that cause or intensify the color of the chromophore by altering the overall energy of the electron system. Textile dyes are generally grouped into 14 different classes¹. These are- i Acid dyes: The largest class of dyes in the Color index is referred to as Acid dyes. Acid dyes are anionic compounds that are mainly used for dyeing nitrogen-containing fabrics like wool, polyamide, silk and modified acryl. Most acid dyes are azo yellow or red anthraquinone or triarylmethane blue or green compounds. Reactive dyes are dyes with reactive groups that form covalent bonds with OH-, NH-, or SH- groups in fibres cotton, wool, silk, nylon. The reactive group is often a heterocyclic aromatic ring substituted with chloride or fluoride. Another common reactive group is vinyl sulphone. In the Color index, the reactive dyes form the second largest dye class with respect to the amount of active entries. Direct dyes are relatively large molecules with high affinity for cellulose fibres. Van der Waals forces make them bind to the fibre. Direct dyes are mostly azo dyes with more than one azo bond. Mordant dyes are fixed to fabric by the addition of a mordant, a chemical that combines with the dye and the fibre. Though mordant dyeing is probably one of the oldest ways of dyeing, the use of mordant dyes is gradually decreasing. They are used with wool, leather, silk, paper and modified cellulose fibres. Most mordant dyes are azo, oxazine or triarylmethane compounds. Sulphur dyes are complex polymeric aromatics with heterocyclic S-containing rings. Dyeing with sulphur dyes involves reduction and oxidation, comparable to vat dyeing. They are mainly used for dyeing cellulose fibres. Vat dyes are water- insoluble dyes that are particularly and widely used for dyeing cellulose fibres. The dyeing method is based on the solubility of vat dyes in their reduced form. Reduced with sodium dithionate, the soluble vat dyes impregnate the fabric. Next, oxidation is applied to bring back the dye in its insoluble form. Almost all vat dyes are anthraquinones or indigoids. Basic dyes are cationic compounds that are used for dyeing acid-group containing fibres, usually synthetic fibres like modified polyacryl. Most basic dyes are diarylmethane, anthraquinone or azo compounds. Disperse dyes are scarcely soluble dyes that penetrate synthetic fibres cellulose acetate, polyester, polyamide, acryl, etc. Dyeing takes place in dyebaths with fine disperse solutions of these dyes. Among these textile dyes " acid dyes, direct dyes, sulphur dyes, azoic dyes, fibre reactive dyes and disperse dyes are considered as toxic substances. Environmental concern Many dyes are visible in water at concentrations as low as 1 mg/L. Textile processing wastewaters, typically with dye content in the range 10 " mg/L-1, are therefore usually highly colored and present an aesthetic problem if discharged in open waters. As dyes are designed to be chemically and photolytically stable, they are highly persistent in natural environments. The release of dyes may therefore present an ecotoxic hazard and introduces the potential danger of bioaccumulation that may eventually affect man by transport through the food chain. Toxicity of dyestuff Dyestuff toxicity has been investigated in numerous researches. Furthermore, research has been carried out to effects of dyestuffs and dye containing effluents on the activity of both aerobic and anaerobic bacteria in wastewater treatment systems².

The acute toxicity of dyestuffs is generally low. The most acutely toxic dyes for algae are " cationic " basic dyes. The chance of human mortality due to acute dyestuff toxicity is probably very low. However, acute sensitization reactions by humans to dyestuff often occur. Especially some disperse dyestuffs have been found to cause allergic reactions, eczema or contact dermatitis. Chronic effects of dyestuffs, especially of azo dyes, have been studied for several decades. Researchers were traditionally mostly focused on the effects of food colorants, usually azo compounds. Furthermore, also the effects of occupational exposure to dyestuffs of human workers in dye manufacturing and dye utilizing industries have received attention. Azo dyes in purified form are seldom directly mutagenic or carcinogenic, except for some azo dyes with free amino groups. However, reduction of azo dyes, i. Various other organs, especially the liver and the kidneys, can, however, also reduce azo dyes. After azo dye reduction in the intestinal tract, the released aromatic amines are absorbed by the intestine and excreted in the urine. The acute toxic hazard of aromatic amines is carcinogenesis, especially bladder cancer. These acyloxy amines can be converted to nitrenium and carbonium ions that bind to DNA and RNA, which includes mutations and tumor formation. The mutagenic activity of aromatic amines is strongly related to the molecular structure. In and in , the International Agency for Research on Cancer IARC summarized the literature on suspected azo dyes, mainly amino-substituted azo dyes , fat-soluble azo dyes and benzidine azo dyes, but also a few sulphonated azo dyes. Most of the dyes on the IRAC list were taken out of production. Generally stated genotoxicity is associated with all aromatic amines with benzidine moieties, as well as with some aromatic amines with toluene, aniline and naphthalene moieties. The toxicity of aromatic amines depends strongly on the spatial structure of the molecules or in other words the location of the amine groups. For instance, whereas there is strong evidence that 2-naphthylamine is a carcinogen, 1-naphthylamine is much less toxic. The toxicity of aromatic amines depends furthermore on the nature and the location of the substituents. As an example, the substitution with nitro methyl or methoxy groups or halogen atoms may increase the toxicity, whereas substitution of carboxyl or sulphonate groups generally lowers the toxicity. As most soluble commercial azo dyestuffs contain one or more sulphonate groups, insight in the potential danger of sulphonated aromatic amines is particularly important. In an extensive review of literature data on genotoxicity and carcinogenicity of sulphonated aromatic amines, it was concluded that sulphonated aromatic amines, in contrast to some of their unsulphonated analogues have generally no or very low genotoxic and tumorigenic potential. The state of Bangladeshi water The increasing urbanization and industrialization of Bangladesh have negative implications for water quality. The pollution from industrial effluents in some water bodies and rivers has reached at an alarming level. The long-term effects of this contamination by organic and inorganic substances, many of them toxic, are severe. In Bangladesh, industrial units are mostly located along the banks of the rivers, which provide transportation for incoming raw materials and outgoing finished products. Unfortunately as a consequence, industrial units drain effluents directly into the rivers without any consideration of the environment. Textile industry is one of the most problematic industries for the water sector. A complex mixture of hazardous chemicals, both organic and inorganic is discharged into the water bodies from these industries, usually without treatment. The Textile Industries The textile industries use vegetable fibres such as cotton, animal fibres such as wool and silk and a wide range of synthetic material such as nylon, polyester and acrylics. The amount of production of natural fibres is approximately equal to the amount of production of synthetic materials. The stages of textile production are fibre production; fibre processing and spinning; yarn preparation; fabrics production; bleaching; dyeing and printing and finishing. Each stages produces waste that requires proper management. The wastewater is typically alkaline and contains solids, oils and potentially toxic organics, such as phenols from dyeing and halogenated organics from bleaching. Dye wastewaters are frequently highly colored and may contain heavy metals such as copper and chromium. As the diagram demonstrates, this historical trend means that established production facilities become more environmentally aware. Over time, they move towards the most efficient mode of treating pollution: Pollution prevention in the textile industry should focus on reducing water use and on more efficient use of process chemicals. Changes to textile production processes that affect type and volume of effluent include the following: Matching process variables e. This can reduce waste by percent. Matching batches to minimize waste at the end of cycle. Avoiding non-degradable or less degradable washing

and scouring chemicals. Using pad batch dyeing. This dyes the fabric at full width. The fabric is passed through containing the dye and between two heavy rollers, which force the dye into the cloth and squeeze the excess dye. This saves up to 80 percent of energy requirements and 90 percent of water consumption. It also reduces dye and salt usage. Using fewer toxic dye carriers and finishing agents. Avoid carriers containing chlorine, such as chlorinated aromatics. Reusing dye solution from the dye bath. Recovering and reusing process chemicals. Controlling the quantity and temperature of the wastewater.

Chapter 5 : Azo dye - Wikipedia

Thomas and Holliday, England, synthesized the first azo dye formed on the fabric by coupling. Vacanceine red formed by treating fabric with naphthol and then dipping in a diazotized amine, a very fast category of dyes.

Table 4 Technological classification of dyes. Group 1 dyes Dyes in this group are characterized by their solubility in water. Consequently they are not particularly fast on washing. The method of application involves only a single stage process. These dyes are soluble in water giving anionic species. They are usually applied at ca K. Whereas wool and other protein fibres degrade readily above this temperature, polyamide fibres for example, the nylons can be treated at K without any harm coming to them Table 4. The pH chosen for the solution in the dyebath depends on the individual properties of the dyes. The lower values are obtained by adding sulfuric acid and higher values by adding solutions of ethanoic acid and ammonium sulfate or ammonium ethanoate. Sodium sulfate may be added to control the diffusion of the dye anions in the fibre structure. By the very nature of the dye structure, ionic bonds, hydrogen bonds and other intermolecular interactions Table 2 will form between the dye and the fibre thus making the dyes fast. An example of a typical acid dye is C. One of the azo groups in this tautomer is present as the ketohydrazone form. However they are duller than the acid dyes because of the presence within the dye structure of a metal atom. Chromium salts are often used although cobalt and nickel salts are also favoured. An example is C. Their application to wool is similar to that for acid dyes, but the pH value is restricted to the range of 4. They are synthesized with sulfonic acid groups to give them solubility in water, dissociating to give sodium cations and the anionic dye species. They are also designed so that they are as linear and planar in structure as possible. This allows the dye to be attached to the cellulosic chains in the fibre, often via intermolecular including hydrogen bonding. They are applied in the dyebath in aqueous solution which contains sodium chloride. The salt reduces the electrical forces of repulsion between the negative charge on the fibre surface and the anionic dye species. Most of the direct dyes are azo compounds, often containing two or three azo groups. The colorant exhibits tautomerism, as there are two hydroxyl groups ortho to the azo groups. One of the tautomers in equilibrium with this form is where there are two ketohydrazone groups. Direct Blue 71, has three azo groups, one of which is present as the ketohydrazone tautomer: Indeed Mauveine is a basic dye. The chromophore is present as a cation and they are used nowadays in dyeing acrylic fibres usually a co-polymer with propenonitrile acrylonitrile and a small amount of a co-monomer which contain sulfonate, $-\text{SO}_3^-$, and carboxylate, $-\text{CO}_2^-$, groups. These are ion-ion interactions Tables 2 and 4. There are about basic cationic dyes whose colours span reds, yellows and blues, with bright strong shades. Some are based on the azo and anthraquinone chromophore systems. Many are also based on arylcarbonium ions. Basic Green 4 known as Malachite Green and C. These are both triarylmethanes, a group of dyes which with relatively small changes in structure produce a range of red, green and violet hues. They owe their colour to the presence of a conjugated system. An example of such a dye is C. Basic Yellow 28 which is a diazacyanine: The dyes are often applied in a solution of an electrolyte, which controls the rate of diffusion in the fibre structure, at temperatures of about K. However they have affinity for hydrophobic fibres, for example polyesters, and are applied as very fine dispersions in water Table 4. Most disperse dyes are azo compounds and can give colours across the spectrum. Some are anthraquinone based dyes for reds, violets, blues and greens. Polyester fibres can be dyed at K under pressure, allowing the use of larger molecular size dye structures which achieve better fastness, for example: The structure shown is the ketohydrazone tautomer. Group 2 dyes Although the dyes in this group are applied by a two stage process which contrasts with the single stage process for Group 1 dyes, the dyes have advantages, in particular with fastness. Blues and greens are also provided by anthraquinone and phthalocyanine structures. As the name of these dyes suggests, they react with the fibre, whether cellulosic cotton or protein wool to form covalent bonds Table 4. The two stages, first dyeing, then reaction, can take place separately or simultaneously. The characteristic structural feature is the presence of one or more reactive groups. The most important reactive groups are the chlorinated triazines and vinylsulfones. One of the three isomers of the simplest triazine is: An example of a dye with a dichlorotriazine group is C. The reaction between the $-\text{OH}$ groups of the cellulose in

the fibre and the -C-Cl groups in the chlorotriazine is by a nucleophilic substitution reaction to form covalent bonds. The sulfone group can be seen in C. In this example, there is no bridging group. The dye reacts with cellulose by addition to the sulfur-oxygen double bond. Reactive dyes, in the aqueous solution, can undergo hydrolysis of the sulfone making it unreactive to the cellulose. This means that unreacted dye, if not washed off properly, will remain on the surface of the fabric giving an apparent colour that will wash out over time. To reduce this problem, dyes have been designed with two different reactive groups of differing reactivity. These dyes offer improved fastness because if one of the groups is hydrolyzed in solution, the other one will react with the hydroxyl groups in the fabric. The first of these included both a chlorotriazine and vinylsulfone groups and an example is C. Besides the two different reactive groups, there is a chromogen and a bridging group. All the reactive dyes have a relatively small molecular size and they also have two or more sulfonic acid groups in the chromogen, leading to a high solubility in water. A proportion of dye species anionic does not react with the fibre and is hydrolyzed and the product must be removed by washing. Figure 3 Jeans are dyed with indigo and a variety of sulfur dyes, the choice depending on the colour desired. By kind permission of Lizzie Hubbard. One type, the indigoid dyes, includes indigo: All vat dyes are insoluble in water. To apply them to a fibre, for example cotton, they are placed in an alkaline solution Table 4. The insoluble dye is reduced to form a colourless leuco anion which is soluble and possesses affinity for the fibre. This is then adsorbed by the fibre, sometimes in the presence of sodium chloride, conditions similar to that for direct dyes. After the dyeing process the original insoluble parent dye is regenerated within the fibre by oxidation, usually using a solution of hydrogen peroxide or simply air: The dyes are insoluble within the fibre structure and therefore have good wash fastness and they also possess high light fastness. Sulphur Black 1 and C. Sulphur Blue 7 are amongst the most widely used sulfur dyes. Like other sulfur dyes, their structures are variable and largely unknown. They provide a range of blacks, browns and dull blues. They are however much cheaper than vat dyes to produce because their preparation by heating various organic compounds with sulfur, is simple. Pigments Pigments are used in the coloration of paints, printing inks, ceramics and plastics. They can be used on a much wider variety of substances than dyes because they are not reliant on water solubility for their application. A pigment is a finely divided solid which is essentially insoluble in its application medium. In most cases the pigment is added to a liquid medium e. The medium is then allowed to solidify by solvent evaporation or cooling and so the pigment molecules become fixed mechanically in the solid state. The chromophores used in pigments are usually the same as those used in dyes but the pigments are large molecules and do not have solubilising groups. They contain groups that form intermolecular bonds that help to reduce solubilities. The larger the molecule, the more opaque the pigment. Figures 4 and 5 The red and yellow colorants are azo pigments C. Pigment Red 57 and C. The blue is the pigment copper phthalocyanine. By kind permission of BASF. Organic pigments generally produce a higher intensity and brightness of colour than inorganic pigments such as chrome yellow lead II chromate VI. Organic pigments exhibit a range of fastness properties that are dependent on the molecular structure and the nature of the intramolecular association in the solid state. An increase in the molecular size of a pigment generally decreases the solubility of the pigment. Many organic pigments are based on azo chemistry and dominate the yellow, orange and red shade areas. An example of a simple monoazo pigment is C. This form is the ketohydrazone tautomer. Copper phthalocyanines provide the majority of blue and green pigments. They are structurally complex but are relatively inexpensive to make. They provide excellent resistance to light, heat, acids and alkalis. Earlier in the unit, the structure of a dye, C.

Azo dyes in purified form are seldom directly mutagenic or carcinogenic, except for some azo dyes with free amino groups. However, reduction of azo dyes, i.e. cleavage of the dye's azo linkage(s), leads to formation of aromatic amines and several aromatic amines are known mutagens and carcinogens.

Azo Dyes What is an azo group? Often, these carbons are part of aromatic systems, but this is not always the case. Most azo dyes contain only one azo group, but some contain two disazo, three trisazo or more². In theory, azo dyes can supply a complete rainbow of colours. However, commercially they tend to supply more yellows, oranges and reds than any other colours. Research is always continuing, though, so that now there are some viable blue azo dyes on the market². The relationship between the colour of an azo dye has been more fully discussed in *The Basis of Colour*. **Azo dye properties** Azo dyes give bright, high intensity colours, much more so than the next most common dye class anthraquinones. They have fair to good fastness properties, but not so good as the carbonyl and phthalocyanine classes. Their biggest advantage is their cost-effectiveness, which is due to the processes involved in manufacture. The general formula for making an azo dye requires two organic compounds- a coupling component and a diazo component. Since these can be altered considerably, an enormous range of possible dyes are available, especially as the starting molecules are readily available and cheap. Furthermore, the simplicity of the reactions mean that the process can be scaled up or down very easily, which is always a key factor in the cost of chemicals. Energy requirements for the reaction are low, since most of the chemistry occurs at or below room temperature. The environmental impact is reduced by the fact that all reactions are carried out in water, which is easy and cheap to obtain, clean and dispose of. As other dye classes become less viable from either an environmental or economic reasons, azo dyes become ever more attractive options. This change from trans preferred to cis can be effected by exposure to UV radiation. This can lead to photochromism, a light-induced reversible colour change in some dyes, for example C. This effect was considered a nuisance and has largely been eliminated by careful development of more stable dyes. But photochromic dyes are beginning to make a comeback in technology like sunglasses and sunroofs in cars². **Tautomerism** This involves the removal of a hydrogen from one part of the molecule, and the addition of a hydrogen to a different part of the molecule. This is common when there is an -OH group ortho or para to the azo group: Tautomeric forms can be identified from their characteristic spectra. Ketohydrazones are normally bathochromic compared to their counterpart hydroxyazo forms. Ketohydrazones also have higher molar extinction coefficients. However, not all azo dyes show tautomerism, and some tautomeric forms are more stable than others². **Synthesis of azo dyes** An overview of azo dye synthesis is shown below: **Stage 1- Diazotisation** This involves a primary aromatic amine, called the diazo component. It is treated in low temperature, acid conditions with sodium nitrite to form an unstable diazonium salt². **Stage 2- Azo coupling** The diazonium salt is reacted with a coupling component for example a phenol or an aromatic amine. This forms the stable azo dye.

Chapter 7 : Azo compound - Wikipedia

Dye: Dye, substance used to impart color to textiles, paper, leather, and other materials such that the coloring is not readily altered by washing, heat, light, or other factors to which the material is likely to be exposed.

Why, then, this name? It has to do with history. The very first artificially produced chemical dye was a produced from aniline aka phenylamine or aminobenzene, and most still use it as a precursor substance. Then again, acetaminophen is also produced from aniline, as are polyurethane, herbicides and nanowire for use as a semiconducting electrode bridge. Chemical structure of aniline Aniline was first isolated from the destructive distillation of indigo, a plant used to produce blue dye, in 1826, it was also isolated from coal tar. Further attempts by several scientists yielded aniline by different processes and, in 1834, C. In these variously named oils were proved to be identical, and thenceforth they took their place as one body, under the name aniline or phenylamine. Chemical structure of Mauveine A The synthetic dye industry grew rapidly as new aniline-based dyes were discovered in the late 1850s and 1860s. These new colors were not only relatively easy to produce, but were quite bright, even garish. The muted dyestuffs of earlier decades gave way to bright prints. Mauve was found to fade very easily—when first applied it is a bright purple, and only after fading is it the light, lavender color that we associate with the name. And mauve gave its name to an entire decade—the 1860s. Purple had once been the rarest and most difficult dye to prepare; Tyrian purple was prepared from the secretions of a predatory sea snail, and was incredibly expensive. With mauve, anyone could afford purple, a color once limited to kings. Aniline itself is a very toxic substance. The dyes we use today are much less toxic than aniline. The greatest risk of disease or injury due to modern acid dyes is by ingestion of or exposure to dye dust. These scenarios are normally confined to textile workers. Whereas the dye itself is normally non toxic, the molecules are metabolized usually in the liver where they may be broken back down to the original intermediates used in manufacture. Many intermediate chemicals used in dye manufacture have been identified as toxic and their use restricted. The chemistry of acid dyes is quite complex. Dyes are normally very large aromatic molecules consisting of many linked rings. Acid dyes usually have a sulfo or carboxy group on the molecule making them soluble in water. Water is the medium in which dyeing takes place. Most acid dyes are related in basic structure to the following: Many acid dyes are synthesized from chemical intermediates which form anthraquinone-like structures as their final state. Many blue dyes have this structure as their basic shape. The structure predominates in the leveling class of acid dye. Although Azo dyes are a separate class of dyestuff mainly used in the dyeing of cotton cellulose fibers, many acid dyes have a similar structure, and most are red in color. Acid dyes having structures related to triphenylmethane predominate in the milling class of dye. There are many yellow and green dyes commercially applied to fibers that are related to triphenylmethane. Acid dyes are thought to fix to fibers by hydrogen bonding, Van der Waals forces and ionic bonding. They are normally sold as the sodium salt therefore they are anionic in solution. See a more in-depth discussion of dye chemistry here. Back to Pysanka Index. Search my site with Google.

Chapter 8 : A History of the International Dyestuff Industry

The Synthesis of Azo Dyes INTRODUCTION Human's love of color reaches back almost to prehistoric times, yet it is not actually until the modern era that the full range of the rainbow has been accessible to the majority of people in.

In chemical terms, their colors are attributed to delocalization of pi electrons. Some azo compounds, such as methyl orange and methyl red, are used as acid-base indicators because their acid and salt forms have different colors. Methyl red is red at pH below 4. Azo pigments are colorless particles typically earths or clays that have been colored using azo compounds. They have excellent coloring properties, again mainly in the yellow to red range, as well as lightfastness that is, colorfast when exposed to light. The lightfastness depends not only on the properties of the organic azo compound, but also on the way they have been adsorbed on the pigment carrier. Azo pigments are advantageous because they are non-toxic. Organic chemistry Azobenzene is the prototypical aryl azo compound. Aryl azo compounds are usually stable, crystalline species. Azobenzene is the prototypical aromatic azo compound. It exists mainly as the trans isomer, but upon photolysis, converts to the cis isomer. Aromatic azo compounds can be synthesized by using an azo coupling reaction, which entails an electrophilic substitution reaction where a aryl diazonium cation attacks another aryl ring, especially those substituted with electron-releasing groups. Owing to this process, some aliphatic azo compounds are utilized as radical initiators. Representative is azobisisobutyronitrile AIBN which is widely used as an initiator in polymerization. Because of their instability, especially for aliphatic ones, care should be taken with the handling of azo compounds or an explosion may occur. Formation by azo coupling An azo compound is formed by a reaction known as an azo coupling. It is an organic reaction between a diazonium compound and an aniline or a phenol. The reaction with phenol may be written as follows: This reaction is called an electrophilic aromatic substitution. The diazonium salt acts as an electrophile, and the activated arene, a nucleophile. The reaction mechanism may be written as follows:

Chapter 9 : Azo compound - New World Encyclopedia

Therefore, they are used as dyes, and are commonly known as azo dyes, an example of which is Disperse Orange 1. Some azo compounds, e.g., methyl orange, are used as acid-base indicators due to the different colors of their acid and salt forms.

Making dyes is difficult at best. If you follow accurate and detailed instructions, the process can be less daunting. Compare it to baking a cake. You follow the recipe exactly, but wind up with a sub-par cake. Maybe your oven was too hot or you waited too long between steps. Even when you follow the recipe, things can go wrong. So how does this compare to dye making? Creating an Azo Dye: These are the simplest of dyes to produce. We crack intermediate chemicals from crude oil, test them, and cause reactions. Sometimes we need multiple reactions to produce the dye product we want. Dye manufacturing consists of five basic steps: You must watch for one factor that influences all these processes: If you use impure or tainted intermediates, your result is contaminated dyes. The same holds true for manufacturing a dye. What you put in is what you get out. **Diazotization** In the first step, we produce a diazonium salt to react with a coupling component. The process involves nitrosation of primary aromatic amines. We do this by introducing a strong acid like HCL and Sodium Nitrite, with ice to control the temperature. After the reaction, we test the product with starch iodide paper and create a blue reaction. The more times we perform a diazo reaction, the different class of dye. These include dye products like disazo, trisazo, and polyazo. **Coupling** To complete the synthesis of an azo dye, the diazonium salt reacts as an electrophile with an electron-rich coupling component, like a phenol or an aniline. This is done through an electrophilic aromatic substitution mechanism. We must control this reaction by monitoring pH, volume, time, and temperature throughout the coupling reaction. An end point test will show if the reaction completed. You achieve this by testing a salted sample of the coupling solution with a diazo or coupling. Normally, a slight excess of either the diazo or coupling exists. Whichever component was in excess will react after performing this test. Once you complete the test and the results look good, we can move to the next step. **Isolation and Filtration** In the isolation-filtration process, you adjust the coupling liquid for pH, salt content, volume, and temperature. Then, filter the coupling. This process separates the liquid from the dyesalt crystals in the coupling liquid. Sometimes the product does not isolate and the coupling goes directly into the spray dryer, completing the drying phase. The isolation-filtration stage produces a paste the consistency of thick mud. **Drying** A common way to dry the paste is to spread it onto trays and place it in a tray dryer. After spreading, the trays go on a rack dryer and dry at a specific temperature. Once dry, we grind it to a specific particle size usually the consistency of flour salt. If we used an alternative drying method, like spray drying, we can skip this step. **Testing the Dye** The last step is to test the dye to ensure it meets specifications for the end product. These include concentration, shade, solubility, and often use-specific tests. Testing is a moment of truth. The question is, will this batch meet the standard? It is the same question we have when making a cake, will we be able to enjoy it? These five steps serve as a basis of what it takes to make one of the most common dye classes. Each dye family has its own set of processes and tests it undergoes to create the end color. Sometimes, the properties of the dye class are more important than the hues. Other times, vice versa. To learn more about dye families and using dyes in your products, click below!