Joseph M. DeSimone, of the University of North Carolina & North Carolina State University & co-founder of Micell Technologies, discovered that polymers having a carbon chain backbone with most or all the hydrogen carbon valences having attached fluorine atoms (fluoropolymers) are soluble in liquid & supercritical CO_2. The solubility of the fluoropolymers in CO_2 is due to the very weak van der Waals forces betn CO_2 molecules & these very weak Vander Waals forces that exist betn the fluorocarbon tails on the copolymer shown in fig 2.).

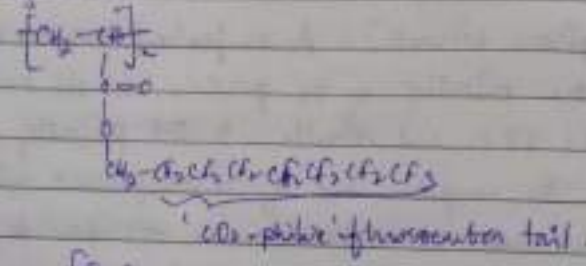


fig 2.

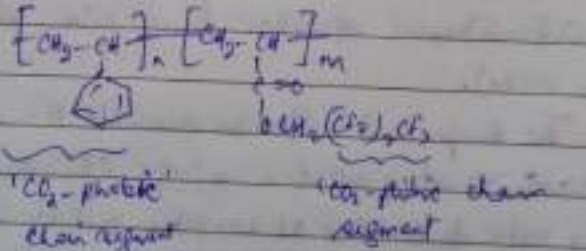


fig 3.

De Simone has created block & graft polymers in which some segments (or blocks are soluble in CO_2, & other segments (or blocks) are insoluble in CO_2. A surfactant for CO_2 might use the combination of a 'CO_2-philic' block comprising the main chain of the polymer with 'CO_2-philic' blocks (a fluoropolymer) attached

grafted onto the main chain. Depending on what type of material one wants to dissolve, the CO_2-philic segment can be made either lipophilic (attracted to fats, greases, and oils) or hydrophilic (attracted to water).

When the copolymer is placed in a medium of liquid or supercritical CO_2, it will arrange itself into a micelle structure. The CO_2-soluble segments surrounds the encases the CO_2 insoluble segment.

By using a surfactant, one can increase the solubility of common industrial materials (waxes, greases, oils, etc) in CO_2. Thus, CO_2 can be used as a solvent for industrial cleaning, with the use of copolymer surfactant having one segment soluble in CO_2 & the other segment (the CO_2-insoluble segment) with an affinity towards a wax, grease or oil. CO_2-insoluble materials such as waxes, greases & oils would become entrapped in the micelle structure & carried away in the liquid or supercritical CO_2 solvent. This technology has the potential to result in the replacement of many ozone-producing & ozone-depleting industrial solvents.

Green Chemistry in Action

This CO_2-surfactant technology is currently being used on a commercial basis by a Micell Technologies. Founded in 1995 by Joseph DeSimone, Timothy Romack & James McClain, Micell Technologies is currently building dry-cleaning machines that use liquid CO_2 & a surfactant to dry-clean clothes, replacing PERC (a solvent which contaminates ground water & is a suspected human carcinogen).

Designing of Environmentally Safe Marine Antifoulant.

Antifoulants (Marine Pesticides).

Unwanted organisms are killed or controlled by pesticides. Chemical pesticides usually act by interfering with a biological function in the target organism.

In the ocean, the hulls of dock pilings are covered with algae & seaweed (soft foulants) & encrusted with barnacles and diatoms (hard foulants). The hull of a ship is constantly immersed in water for several years & so buildup of these same marine organisms can lead to a significant hydrodynamic drag on the ship. This drag on a ship impedes its passage through the water resulting in increased fuel usage, causing higher operational & environmental costs.

Use of antifoulants (Pesticides) to control the growth of Marine Organisms :

Organotin antifoulants :

In order to inhibit the attachment and growth of marine organisms, the hulls of ships are usually treated with chemical compounds known as antifoulants. These are generally dispersed in the paint as it is applied to the hull. Organotin compounds particularly tributyltin oxide (TBTO) are very effective antifoulants (used in agriculture,

wood & plastics industries etc).

The effectiveness of TBTO is a result of the fact that it gradually leaches from the hull killing the fouling organisms in the surrounding area.

TBTO & PBes organotin antifoulants have relatively long half-lives in the environment (half-life of TBTO in seawater is > 6 months).

Tributyltin oxide

These significant conc^n of these compounds can be found in ocean sediments as well as the water & they tend to bioconcentrate in marine organisms. Thus, organotins are persistent pollutants & are chronically toxic to marine life at the ppt level and may enter the food chain. TBTO causes deformations in the thickness of oyster shells, sex changes in whelks & imposex in snails. The immune systems in dolphins, fish & other marine organisms may be compromised as a result of the bioconcentration of organotin compounds. Because of these environmental problems & concerns, organotins are banned out globally.

Green Chemistry: An Environmentally Preferable Antifoulant:

Rohm & Haas Company developed SEA-NINE 211 marine antifoulants. The active ingredient in Sea-Nine 211 are 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI), is a member of the isothiazolone family of antifoulants.

DCOI

DCOI works by maintaining a hostile growing environment for marine organisms. When organisms attach to the hull (treated with DCOI), proteins at the point of attachment will be hull bound with the DCOI. This bond with the DCOI prevents the use of these proteins for their metabolic processes. The organisms then detaches itself & searches for a more hospitable surface on which to grow.

Reducing the environmental risk with ~~[illegible]~~ dose-response

Environmental risk is a function of toxicity & exposure:

ENVIRONMENTAL RISK = F (TOXICITY AND EXPOSURE).

Environmental risk can be mitigated by reducing the toxicity of a compound or by reducing the exposure to the compound. DCOI was found to be active against algae & diatoms at conc. of around 10 ppb & barnacle larvae at ppm levels. However the environmental risk of DCOI is minimal because only organisms in contact with the ship's hull are exposed to toxic levels of DCOI. Although DCOI is stable as part of the coating on a ship, when it is released (leached) closely from the hull of the ship it rapidly degrades (when in contact with seawater) to compounds that are essentially nontoxic. This decomposition is a result of microorganisms naturally present in the seawater. The half life of DCOI in water at pH 7 is greater than ~120 hrs, while in natural seawater the half life drops to less than an hour. This rapid biodegradation leads to

environmental conc. of a compound in the environment DOP DCOI that are below the acute toxicity level.

The rapid biodegradation of DCOI is accompanied by rapid partitioning of DCOI to the soil/sediment due to low solubility of DCOI in water. The adsorption of DCOI by the soil/sediment decreases its ~~bioavail~~ bioavailability + also adds to the bioavailability of DCOI. It has a bioconcentration factor of only 0.86 compared to 1500 for TBTO.

In order to calculate the environmental risk of a substance Reinecke & Nel consider the ratio of the predicted environmental conc. (PEC) of a compound & the bioconcentration of DCOI is not expected to reach levels in marine organisms that would lead to excess concentration of a compound in the environment at which predictions indicate there will be no effect on the organisms (predicted no effect concentration, PNEC). The ratio of PEC/PNEC is known as.

$$RQ = PEC/PNEC.$$

The risk quotient (RQ) and as the risk quotient gets smaller the less the risk there is associated with the substance. The RQ of a substance should be <1. The RQ of DCOI ranges from 0.029 to 0.36 indicating the environmental conc. of DCOI should pose little risk of toxicity to marine organisms. Conversely the range of RQ for organotin antifoulants is 15-430 indicating a significant risk to marine life.

Colorants (dyes & pigments) are compounds which absorb light in the visible portion of the electromagnetic spectrum by filtering out specific wavelengths of white light. They produce colors due to excitation of electrons within the colorant compound. Many organic & inorganic compounds have electronic properties that enable them to act as dyes & pigments.

Many inorganic dyes & pigments are based on heavy metals which are toxic to both human being & the environment. The organic alternatives carry similar toxicity risks. The synthesis of organic pigments & dyes often exposes workers to dangerous solvents & reagents. & the colorants themselves (or the products of their degradation) can be carcinogenic & toxic compound.

Engelhard Corporation (now BASF Corporation) has produced a family of synthetic organic pigments. They can be synthesized in aqueous media & provide stronger color properties than other pigments. Pigment pigments are more resilient to degradation than their common counterparts, & when they do degrade, no harmful or bioaccumulative substances are expected to be formed.

Many heavy metals such as chromium, cadmium & lead are used extensively in inorganic pigments. Chronic exposure to these metals causes physical damage, neurological disorders & even cancers. Over 95% of the pigments used

pesticides today contain heavy metals.

Pigments are the colorants composed of particles that are insoluble in the application medium. They are intended to color the whole or a portion of a substrate. In the other hand, dyes are colorant substances that are at least partially soluble in their intended substrate. Meaning all inorganic colorants are pigments.

Like any colored compounds, heavy metal-based pigments with big absorbing (or reflecting) portions of the visible electromagnetic spectrum. The visible portion of the electromagnetic spectrum contains all light with wavelength between 400 & 700 nm. When the human eye sees light with all of these wavelengths, we perceive it to be white.

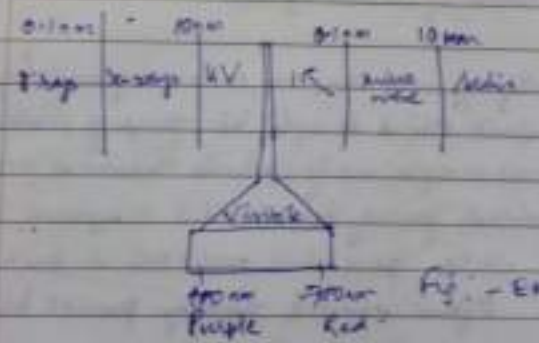


Fig. - EM spectrum

$E = \frac{hc}{\lambda}$, λ = wavelength of light, h = Planck's constant $= 6.626 \times 10^{-34}$ Js

c = speed of light $= 3 \times 10^{8}$ m/s

Compound color

electromagnetic energy which is equal to the energy needed to lift a higher energy state. In colored compounds, light in the visible

position of the electromagnetic spectrum provides the energy to promote an electron from a "ground state" configuration to an "excited state configuration". The light which causes this excitation must have energy equal to the difference in energy (ΔE) between the ground and excited electronic states. In this way only specific colors of visible light (with specific energies & wavelengths) are absorbed by a compound, which causes us to see only the colors of the reflected - unabsorbed light.

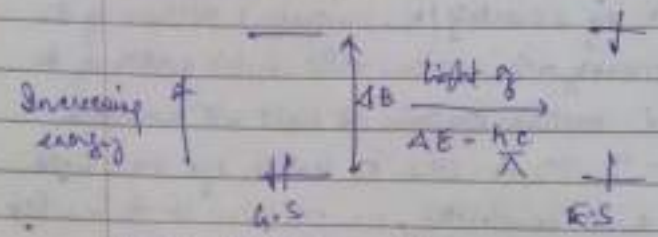


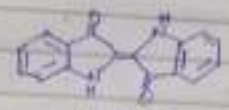
Fig :- Excitation of electrons by light

The geometry of metal complexes causes degenerate (equal energy) atomic orbitals to split into groups of orbitals with different energies, making electronic transitions possible. Organic colorants generally have extended π systems & nonbonding electron pairs which participate in such transitions. Organic colorants typically provide brighter colors than inorganic colorants, but are more easily damaged thermally & photochemically. The ability of a colorant to retain its coloring over time is referred to as its lightfastness.

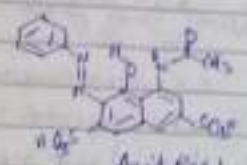
However, organic colorants are not necessarily green alternatives to inorganic pigments. The production & application of organic colorants usually

chemicals, and the synthetic procedures usually involve the use of volatile organic solvents.

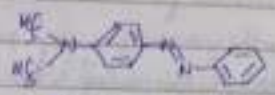
The use of toxic substances in organic solvent synthesis has even halted the production of some organic colorants, such as the azo based on benzidine. Benzidine, a known carcinogen, was once used in widespread manufacture of organic colorants. The manufacturing of some organic colorants often lead to the generation of high volumes of wastes such as phosphates. Phosphate waste into natural water can cause algal blooms (uncontrolled growth of aquatic microorganisms), which deplete dissolved oxygen in aquatic ecosystem & thus suffocate other aquatic life.



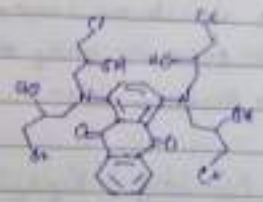
Indigo



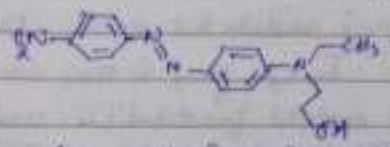
Acid Red 1



Butyl Yellow



Reactive Red 6



Disperse Red Scarlet B (3).

Fig: Examples of common organic colorant.

Many organic colorants are toxic. Butter Yellow, used to give butter its aesthetic yellow colour is a carcinogen.

Diarylide pigments are made from halogenated precursors such as dichlorobenzidine. It undergo thermal degradation at temperatures as low as 290°C. The degradation produces dichlorobenzidine, which is an animal carcinogen.

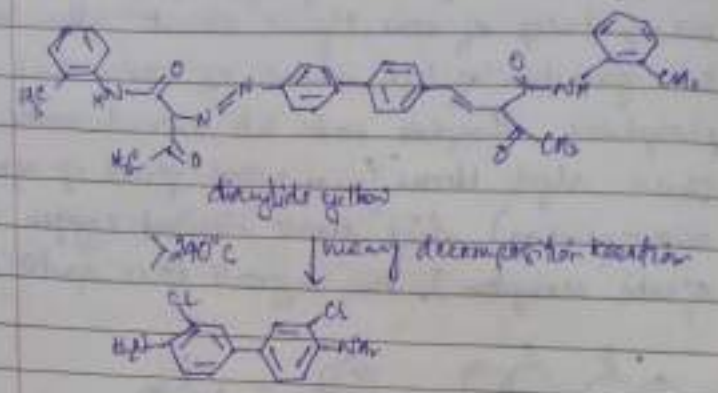


Fig: Thermal decomposition of diarylide yellow.

While less-harmful alternative replacements for these dangerous organic colorants are known, they are generally poorer colorants (e.g. more easily degraded) & have higher production costs.

Colour Chemistry: Rightfast pigments:

Azo compounds are organic molecules that contain at least one "azo group" (-N=N-). The azo group in these colorants often connects to two aromatic functionalities, creating an extended, conjugated network of π electrons. This network results in the formation of molecular orbitals with energies as shown in Fig. A

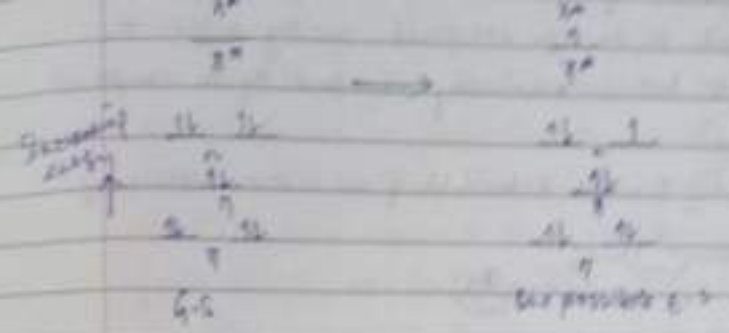


Fig A : Qualitative M.O. diagram for π & π* antibonding orbitals in azobenzene.

Excitation of electrons from the higher bonding energy (bonding) to the higher energy (antibonding) orbitals results from the absorption of light in the visible or UV range.

Azo compounds can exist as both (E) & (Z) isomers.

(E)-azobenzene (Z)-azobenzene

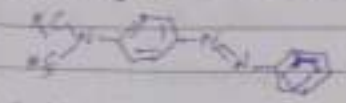
Fig : Isomerization of azobenzene

UV or visible light provides the isomerization between these two forms, which often results in discoloration of the dye as pigment. For azobenzene, in the absence of UV (or near-UV) light, the equil. lies almost exclusively in favour of the (E) isomer. However, when azobenzene is irradiated with 405 nm light, 88% of the (Z) isomer is formed.

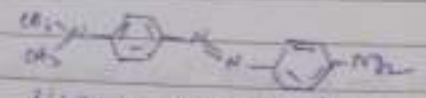
The isomerization of (E) & (Z) forms is an equilibrium and so each is a dynamic process. E.g. the azo dye disperse fast blacklit & discolours & fades when exposed to daylight, but returns its original color when placed in the dark.

The presence of electron-donating or electron-withdrawing substituents on an azo compound greatly affects the wavelength that is maximally absorbed by the compound (λ_{max}).

Fig 8. The substitution of an electron withdrawing



Butter yellow, λ_{max} = 452 nm



N-methyl butter yellow, λ_{max} = 478 nm.

Fig 8

Nitro substituent at the 4' position shifts the λ_{max} of 1 by +26 nm. This results in a color change from yellow to orange-red. The effect that a substituent has on a azo dyes is based on substituent's electron affinity, electronic structure, steric interactions & position on the chromat.

In 2019, the Engelhard Corporation earned a Distinctive Green Chemistry Challenge Award for their production of Rightfit pigments.

Rightfit pigments are azo pigments that are more heat-stable & less harmful than comparable, classical azo pigments. Moreover, it provide improved color strength, thus allowing one to color a substance using less pigment.

The synthesis of rightfit azo pigments are carried out in aqueous media. This prevents the generation of large volume of waste organic solvent, limits the exposure of workers to dangerous organic solvents

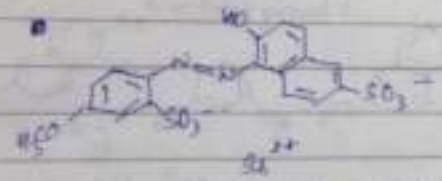
during manufacture & avoid the evolution of volatile organic vapors.

Rightfit pigments have structures like to common food colorants (most are food colorants & the Rightfit pigments are fig C). While they are not designed to be ingested, the FDA has approved Rightfit pigments for 'indirect food contact' applications. These pigments have been specially formulated to be very insoluble in lipids. Because of this, Rightfit pigments that are accidentally ingested are not bioaccumulate in fatty tissue.

Food red (4)

Pigment Red (5)

48:2



Rightfit Pink (6)

Fig C: Comparison of a Rightfit pigment to a common food dye & a classical azo pigment.

Most of the Rightfit pigments are formulated without halogenated substituents & photolytic scission of the azo linkages in Rightfit pigments produces aromatics which are considered safe by the EPA.

Rightfit pigments are stable at higher temp than classical azo pigments. Eg. Pigment Red 48:2 (5) is only stable at temp. below 200°C, whereas the Rightfit hues are stable up to 260°C.

toxic pigments such as cadmium-, lead- & chromium-based compounds or the diarylide, dichlorobenzidine-based organics.

Ingelhard has produced 14 different pigments that are red, orange, yellow or even purple. These modifications usually involve the bring substituents, protonating an anionic substituent or changing the laking metal (Fig D). Rightfast pigments are all structurally similar, they can be easily shade in the red/orange/yellow colour space. The presence of anionic groups on halogenated aromatics has been shown to facilitate the reductive dehalogenation of these species in the environment.

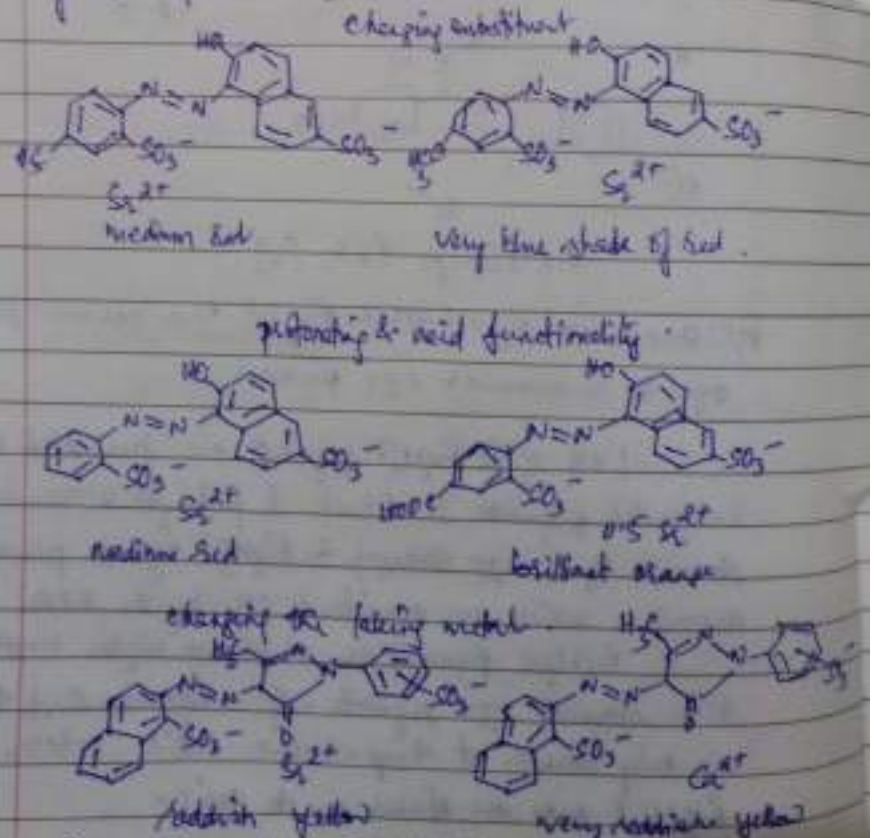


Fig D: Examples of Rightfast pigment modifications.

Green chemistry in Action:

Rightfit pigments are currently most extensively in the production of colored plastics, such as soft drink packaging, food containers, detergent bottles, & other household items. The distributing product company Rightfit pigments has spread to Europe & Asia.

In 1995, Rockwood's production of lead; chromium, & cadmium-based pigments was as high as 65 million pounds per year. With the introduction of their Rightfit pigments, that no. was reduced to less than 1.2 million pounds in 2002, & the production of these pigments was entirely phased out in 2004.

An efficient, green synthesis of a compostable & biodegradable plastic (poly lactic acid) made from corn.

Polylactic acid is a plastic that can be made from starch found naturally in plants. It can be used in many applications, including packaging, fabrics and biomedical implants. The material is fully compostable & can be closed-loop recycled back into pure starting materials including polylactic acid. Natureworks LLC has developed a method for producing polylactic acid from corn. This synthesis not only uses a renewable resource to produce the monomer. It also avoids using the organic solvents common to most synthesis of petrochemical-based polymers.

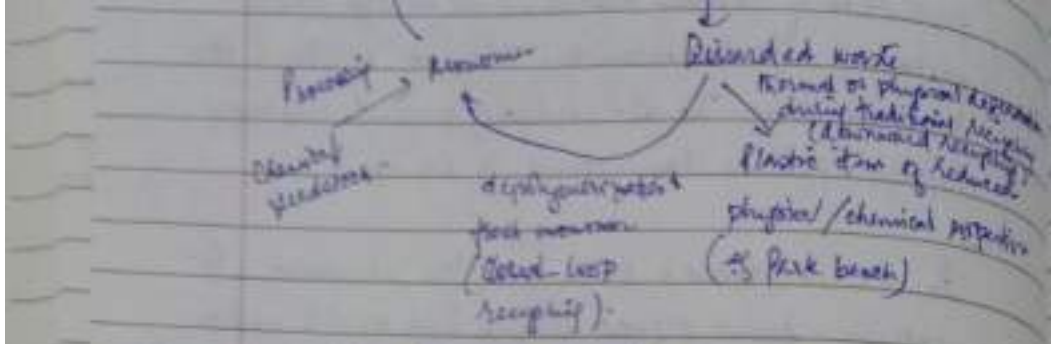


fig 1: Methods of plastic recycling.

Because of contamination & thermal degradation, most plastic products are downcycled/recycled into a product with inferior properties. Eg. a sized plastic bottle that is recycled does not normally return to the consumer as a fresh drink bottle, but rather as an item such as garden pottery or a plastic chair. Downcycled recycling prevents the bottle from entering a landfill, but fresh monomers (from a nonrenewable resource) is still required to create a new bottle.

To circumvent these issues, many polymer chemists & materials scientists have focused their efforts on producing greener plastics. Their goals include the use of renewable feedstocks, the introduction of 'programmed degradability' so the item's lifetime to degradation more closely matches its objective as intended, and a used plastic could be easily depolymerized into its constituent monomers, and could then produce a fresh, virgin polymer from these reclaimed precursors. This process would prevent the degradation in quality caused by more conventional

recycling. In such a scheme, for example a beverage container used today could be closed-loop recycled (Fig. 1) back into a new one.

Green Chemistry : Nature Works Polylactic Acid :
In November 2001, NatureWorks LLC (formerly Cargill Dow LLC) began commercial production of polylactic acid (PLA) @ at a newly commissioned plant located in Blair, Nebraska (Fig 2). PLA is a polymer manufactured from lactic acid @, a small organic molecule that is found naturally in living organisms & is produced through the anaerobic fermentation of glucose &). Lactic acid can be produced commercially from starch plant material (such as corn) & can be polymerized to PLA. PLA is one of a growing no. of biopolymers receiving increased interest in the chemical industry & wider communities. PLA boasts such as annually renewable feedstocks, compostability & the opportunity for closed-loop recycling.

Due to its biocompatibility, the medical community has used PLA for many years in limited quantities to make objects such as bone screws, sutures, surgical staples & tissue scaffolding. The high cost associated with PLA synthesis prohibited its use in products.

PLA physical properties (which include high gloss, clarity, printability, heat-sealability, oil and grease resistance, and its ability to act as a flavor & odor barrier) are comparable or superior to more common everyday plastics such as polystyrene (PS) & polyethylene terephthalate (PETE). These characteristics make PLA a good candidate for use in such items such as films, fibers, drink bottles,

kitchen plates & food storage containers. PLA usually can be composted in under 60 days. It is a popular material from which to make compost bags.

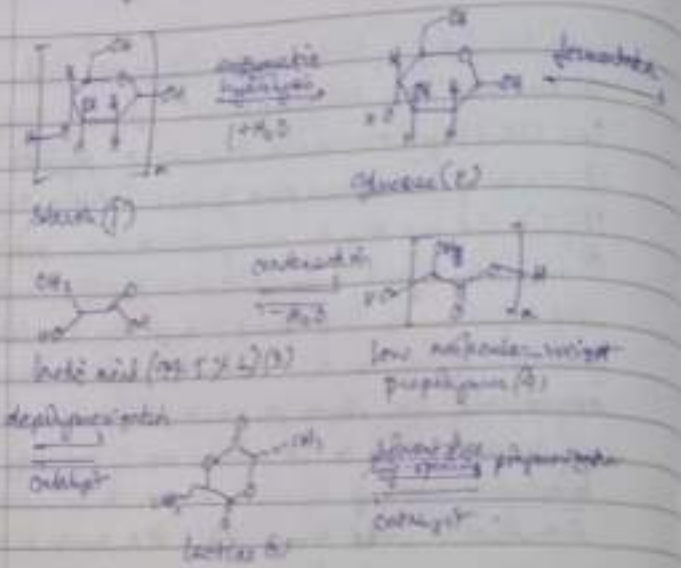
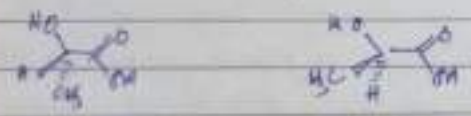


Fig 2 : Nature Works LLC production of PLA from starch.

The process for producing PLA designed by Nature Works received Presidential Green Chemistry Challenge Award in 2002. It employs starch harvested from corn. Corn is the most widely available source of starch (1) in the U.S. Starch is a biopolymer produced in plants by the linking of glucose molecules. Glucose is the product of photosynthesis & therefore we might consider the actual feedstock for PLA to CO_2 & water

The NatureWorks process begins by heating water enzymatically with the corn-derived starch (1), which cleaves the starch glycosidic linkages to form glucose (2), the monomer of starch. The glucose is then converted into lactic acid via fermentation. This process involves the generation of pyruvate (as in glycolysis), which is then converted into lactic acid. The lactic acid produced in this way is enantiomerically enriched, with 99.5% in the L form. Fig (3).



L-lactic acid D-lactic acid

Fig 3 : Isomers of lactic acid.

Lactic acid is then polymerized into oligomeric prepolymer (4) in a mild, solvent-less condensation polymerization.

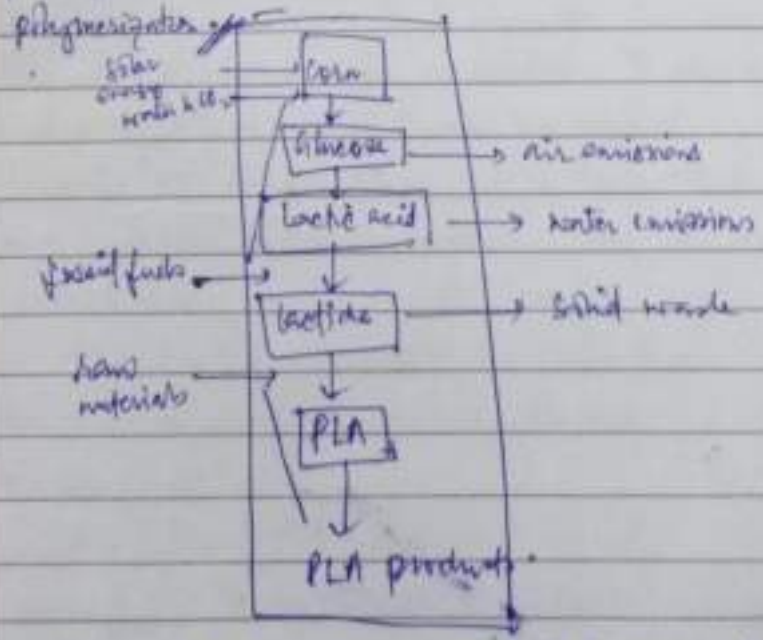


Fig :- FD of NatureWorks PLA production