ACHARYA N. G. RANGA AGRICULTURAL UNIVERSITY

B. Tech (Food Technology)

Course No.: FDST 213 Food Additives

Credit Hours: 2 (1+1)

THEORY STUDY MATERIAL

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A) Theory Lecture Outlines

1. Introduction: What are Food Additives? - Role of Food Additives in Food Processing - functions - Classification - Intentional & Unintentional Food Additives
2. Toxicology and Safety Evaluation of Food Additives - Beneficial effects of Food Additives / Toxic Effects - Food Additives generally recognized as safe (GRAS) - Tolerance levels & Toxic levels in Foods - LD 50 Values of Food additives.
3. Naturally occurring Food Additives - Classification - Role in Food Processing – Health Implications.
4. Food colors - What are food colors - Natural Food Colors - Synthetic food colors - types - their chemical nature - their impact on health.
5. Preservatives - What are preservatives - natural preservation - chemical preservatives – their chemical action on foods and human system.
6. Anti-oxidants & chelating agents - what are anti oxidants - their role in foods - types of antioxidants - natural & synthetic - examples - what are chelating agents - their mode of action in foods - examples.
7. Surface active agents - What are surface active agents - their mode of action in foods - examples.
8. Stabilizers & thickeners - examples - their role in food processing.
9. Bleaching & maturing agents: what is bleaching - Examples of bleaching agents - What is maturing - examples of maturing agents - their role in food processing.
10. Starch modifiers: what are starch modifiers - chemical nature - their role in food processing.
11. Buffers - Acids & Alkalis - examples - types - their role in food processing.
12. Sweeteners - what are artificial sweeteners & non nutritive sweeteners - special dietary supplements & their health implication - role in food processing.
13. Flavoring agents - natural flavors & synthetic flavors - examples & their chemical nature - role of flavoring agents in food processing.
14. Anti-caking agents - their role in food processing
15. Humectants - definition on their role in food processing.
16. Clarifying agents - definition examples - their role in food processing
Lecture1

Food Additives-Introduction

Definition:

Food additives are substances which are added to food which either improve the flavor, texture, colour or chemical preservatives, taste, appearance or function as processing aid. Food additives as non-nutritive substances added intentionally to food, generally in small quantities, to improve its appearance, flavor, texture or storage properties.

A broad definition of “food additive” is any substance the intended use of which results, directly or indirectly, in it’s becoming a component of or otherwise affecting the characteristic of any food, and which is safe under the condition of its use.

Need for Food Additives:

1. Additives provide protection against food spoilage during storage transportation, distribution or processing. Also, with the present degree of urbanization, it would be impossible to maintain food distribution without the processing.

2. A number of factors have led to the demand for foods with built-in preparation of “convenience” foods. The “convenience food revolution” would not have been possible without food additives.

3. Many of these chemical additives can be manufactured so that foods can be “fortified” or “enriched”. Potassium iodide, for instance, added to common salt can eliminate goiter, enriched
rice or bread with B-complex vitamins can eliminate pellagra, and adding vitamin D to cow milk prevents rickets.

4. Many foods, particularly those with high moisture contents, do not keep well. All foods are subjected to microbial attack. Fats or oily foods become rancid, particularly when exposed to humid air. The conversation of the quality of foods against agents causing such deterioration of food requires the addition of preservatives. Additives are also used to colour foods, add flavor, impart firmness, and retard or hasten chemical reaction in food.

5. The use of food additives is to maintain the nutritional quality of food, to enhance stability with resulting reduction in waste, to make food more attractive, and to provide efficient aids in processing, packaging and transport.

**Classification:**

Over 3,000 different chemical compounds are used as food additives. They are categorized into different groups. A few types of additives are indicated below.

1. **Anti-oxidants**

   An anti-oxidant is a substance added to fats and fat-containing substances to retard oxidation and thereby prolong their wholesomeness, palatability, and, sometimes, keeping time. An anti-oxidant should not contribute an objectionable odour, flavor, or colour, to the fat or to the food in which it is present. It should be effective in low concentrations, and be fat soluble. Also, it should not have a harmful physiological effect. Some anti-oxidants used in foods are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and teriarybutyl hydroquinone (TBHQ), which are all phenolic
substances. Thiodipropionic acid and dilauryl thiodipropionate are also used as food anti-oxidants. The Joint FAO/WHO Expert Committee on Food Additives has recently considered the Acceptable Daily Intakes (ADIs) of BHA and BHT and set them at 0-0.5 mg/kg body weight for BHA and 0-0.3 mg/kg body weight for BHT. Naturally occurring substances that act as anti-oxidants are tocopherols. The tocopherols act as biological anti-oxidants in plant and animal tissues, but they are rarely used as additives because they are more expensive than synthetic anti-oxidants.

2. Chelating Agents

Chelating agents are not anti-oxidants. They serve as scavengers of metals which catalyze oxidation. Recommended usage levels for citric acid typically vary between 0.1 and 0.3 per cent with the appropriate anti-oxidant at levels ranging between 100 and 200 ppm)

EDTA is a chelating agent permitted for use in the food industry as a chemical preservative. Calcium disodium EDTA and disodium EDTA have been approved for use as food additives by the United States Food and Drug Administration.

3. Colouring Agents
These include colour stabilizers, colour fixatives, colour fixatives, colour retention agents, etc. They consist of synthetic colours, synthesized colours that also occur naturally, and other colours from natural sources. Even though colours add nothing to the nutritive value of foods, without certain colours most consumers will not buy or eat some foods. Thus, colours are frequently added to restore the natural ones lost in food processing or to give the preparations the natural colour we expect. A number of natural food colours extracted from seeds, flowers, insects, and
foods, are also used as food additives. One of the best known and most widespread red pigment is bixin, derived from the seed coat of Bixa orellana, the lipstick pod plant of South American origin. Bixin is not considered to be carcinogenic. The major use of this plant on a world-wide basis, however, is for the annatto dye, a yellow to red colouring material extracted from the orange-red pulp of the seeds. Annatto has been used as colouring matter in butter, cheese, margarine, and other foods. Another yellow colour, a carotene derived from carrot, is used in margarine. Saffron has both flavouring and colouring properties and has been used for colouring foods. Turmeric is a spice that gives the characteristic colour of curries and some meat products and salad dressings. A natural red colour, cochineal (or carnum) obtained by extraction from the female insect (Coccus cacti), grape skin extract, and caramel, the brown colour obtained from burnt sugar, are some natural colours that are used as food additives.

Curing Agents

These are additives to preserve (cure) meats, give them desirable colour and flavor, discourage growth of micro-organisms, and prevent toxin formation.

Sodium nitrite has been used for centuries as a preservative and colour stabilizer in meat and fish products. The nitrite, when added to meat, gets converted to nitric oxide, which combines with myoglobin to form nitric oxide myoglobin (nitrosyl myoglobin), which is a heat-stable pigment. The curing also contributes flavor to the meat. In addition, nitrite curing inhibits the growth of Clostridium and Streptococcus, and also lowers the temperature required to kill C.botulinum.
**Emulsifiers**

Emulsifiers are a group of substances used to obtain a stable mixture of liquids that otherwise would not or would separate quickly. They also stabilize gas-in-liquid and gas—in-solid mixtures. They are widely used in dairy and confectionery products to disperse tiny globules of an oil or fatty liquid in water. Emulsifying agents are also added to margarine, salad dressings, and shortenings. Peanut butter contains up to 10 percent emulsifiers.

**Flavours and Flavour Enhancers**

Flavouring additives are the ingredients, both naturally occurring and added, which give the characteristic flavor to almost all the foods in our diet. Flavour enhancers are not flavours themselves but they amplify the flavours of other substances through a synergistic effect. Flavour and flavor enhancers constitute the largest class of food additives.

Natural flavor are substances, such as spices, herbs, roots, essences, and essential oils, have been used in the past as flavor additives. The flavours are in short supply and the amount of flavor substances in them is very tiny. It would take about tonne of many spices to produce 1 g of the flavor substances, and in some cases only 0.1 g can be extracted. Natural food flavours are thus being replaced by synthetic flavor materials.

The agents responsible for flavor are esters, aldehydes, ketones, alcohols, and ethers. These substances are easily synthesized and can be easily substituted for natural ones. Typical of the synthetic flavor additives are amyl acetate for banana, methyl
anthranilate for grapes, ethyl butyrate for pineapple, etc. Generally, most synthetic flavours are mixtures of a number of different substances. For example, one imitation cherry flavor contains fifteen different esters, alcohols, and aldehydes.

One of the best known, most widely used and somewhat controversial flavor enhancers is monosodium glutamate (MSG), the sodium salt of the naturally occurring amino acid glutamic acid. This is added to over 10,000 different processed foods. This has been in use in Chinese and Japanese cooking for centuries, and was extracted from seaweeds and soya bean. About 65 years ago, a Japanese named Ikeda discovered that the flavouring from these is MSG and that it has an attractive meat-like flavor. MSG is now manufactured on a large scale all over the world, and especially in Japan.

MSG is generally recognized as safe. However, it was reported some time back that MSG injected to young mice resulted in brain damage. Also, some individuals experience symptoms often comparable to those of heart attack, when served with food containing large amounts of MSG. The matter has now been thoroughly investigated, and it has been concluded that there is no risk in its use. However, MSG which was being added to baby foods is now discontinued, as its benefits to babies are dubious.

Yeast extract has the same flavor enhancing property as MSG. It is found that, in this case, the flavor enhancing substances are the ribonucleotides. These are ten times more powerful than MSG.
Flour Improvers

These are bleaching and maturing agents; usually, they both bleach and “mature” the flour. These are important in the flour milling and bread-baking industries. Freshly milled flour has a yellowish tint and yields a weak dough that produces poor bread. Both the colour and baking properties improve by storing the flour for several months before making bread.

Chemical agents used as flour improvers are oxidizing agents, which may participate in bleaching only, in both bleaching and dough improvement, or in dough improvement only. The agent that is used only for flour bleaching is benzoyl peroxide \((C_6H_5CO)_2O_2\). This does not influence the quality of dough. Materials used both for bleaching and improving are chlorine gas, \((Cl_2)\); chlorine dioxide, \((ClO_2)\); nitrosyl chloride, \((NOCl)\); and nitrogen di and tetra oxides, \((NO_2 and N_2O_4)\). Oxidizing agents used only for dough improvement are potassium bromate, \((KBrO_3)\); potassium iodate, \((KIO_3)\); Calcium iodate, \([Ca(IO_3)_2]\); and calcium peroxide, \((CaO_2)\).

Humectants

Humectants are moisture retention agents. Their functions in foods include control of viscosity and texture, bulking, retention of moisture, reduction of water activity, control of crystallization, and improvement or retention of softness. They also help improve the rehydration of dehydrated food and solubilization of flavor compounds.

Polyhydroxy alcohols are water soluble, hygroscopic materials which exhibit moderate viscosities at high concentrations in water and are used as humectants in foods. Some of them are propylene
glycol (CH₃.CO.H.CH₂.OH), glycerol, and sorbitol and mannitol [CH₂.OH (CHOH)₄ CH₂.OH]. Polyhydric alcohols are sugar derivatives and most of them, except propylene glycol, occur naturally.

**Anti-caking Agents**

Anti-caking agents help prevent particles from adhering to each other and turning into a solid chunk during damp weather. They help free flowing of salt and other powders.

**Leavening Agents**

Leavening agents produce light fluffy baked goods. Originally, yeast was used almost exclusively to leaven baked products. It is still an important leavening agent in bread making. When yeast is used, ammonium salts are added to dough to provide a ready source of nitrogen for yeast growth. Phosphate salts (sodium phosphate, calcium phosphate) are added to aid in control of pH.

**Nutrient Supplements**

Nutrient supplements restore values lost in processing or storage, or ensure higher nutritional value than what nature may have provided. When foods are processed, there may be loss of some nutrients and additives may be added to restore the original value. For example, to produce white flour, wheat is milled in such a way as to remove the brown coloured part of the grain, which is rich in vitamins and minerals. To restore the nutritive value, thiamine, nicotinic acid, iron and calcium, are added to the flour. Similarly, vitamin C is added to canned citrus fruits to make up the loss of the vitamin during processing.

**Non-nutritive Sweeteners**
In many ways, sucrose is an ideal sweetener; it is colourless, soluble in water, and has a “pure” taste, not mixed with overtones of bitterness or saltiness. But it is rich in calories. Diabetics and overweight, who must restrict their intake of sugar, must have an alternative to sucrose. Thus, synthetic non-nutritive sweeteners, having less than two per cent of the calorific value of sucrose, for equivalent unit of sweetening capacity came into use.

The first synthetic sweetening agent used was saccharin (sodium ortho benzene sulphonamide or the calcium salt), which is about 300 times sweeter than sucrose in concentrations up to the equivalent of a 10 per cent sucrose solution.

Acesulfame K is used in baked goods, chewing gum, gelatin desserts, and soft drinks. It is about 200 times sweeter than sugar. Aspartame is used in “Diet” foods, including soft drinks, drink mixes, gelatin desserts, and low calorie frozen desserts. Aspartame is produced from two amino acids—aspartic acid and phenylalanine—and is 180 times sweeter than sucrose.

**pH Control Agents**

These include acids, alkalis and buffers. They not only control the pH of foods but also affect a number of food properties such as flavor, texture, and cooking qualities.

**Preservatives**

A preservative is defined as any substance which is capable of inhibiting, retarding, or arresting, the growth of micro-organisms, of any deterioration of food due to micro-organisms, or of masking the evidence of any such deterioration. It is estimated
that nearly 1/5 of the world’s food is lost by microbial spoilage. Chemical preservatives interfere with the cell membrane of micro-organisms, their enzymes, or their genetic mechanisms. The compounds used as preservatives include natural preservatives, such as sugar, salt, acids, etc, as well as synthetic preservatives.

**Stabilizers and Thickeners**

These compounds function to improve and stabilize the texture of foods, inhibit crystallization (sugar, ice), stabilize emulsions and foams, reduce the stickiness of icings on baked products, and encapsulate flavours. Substances used as stabilizers and thickeners are polysaccharides, such as gum Arabic, guar gum, carrageenan, agar-agar, alginic acids, starch and its derivatives, carboxy methylcellulose and pectin. Gelatin is one non-carbohydrate material used extensively for this purpose. Stabilizers and thickeners are hydrophilic and are dispersed in solution as colloids. These swell in hot or even cold water and help thicken food. Gravies, pie fillings, cake toppings, chocolate milk drinks, jellies, puddings and salad dressings, are some among the many foods that contain stabilizers and thickeners.

**Other Additives**

There are a number of food additives that provide functions other than those indicated above. Clarifying agents like bentonite, gelatins, synthetic resins (polyamides and poly vinyl pyrrolidone) are used to remove haziness or sediments and oxidative deterioration products in fruit juices, beers and wines. Enzymes are added to bring about desirable changes; rennin for producing curd and cheese, papain for tenderizing meat, and pectinase for clarifying beverages. Firming agents like aluminium
sulphates and calcium slats are used to keep the tissues of fruits and vegetables crisp. Freezing agents like liquid nitrogen and dichloro fluoro methane, which are extremely volatile and rapidly evaporate at ordinary temperatures, are used to chill foods. Solvents like alcohol, propylene glycol and glycerine are used to dissolve suspended flavours, colours, and many other ingredients. Packing gases, such as inert gases, are added to packets of instant foods to prevent oxidative and many other changes.

Unintentional Additives

The unintentional incorporation of chemicals into food is as widespread as intentional addition and may present health hazards. The sources of contamination are radioactive fall-out, thousands of chemicals used in agricultural production, animal food additives, and accidental contaminants during food processing.

Radio-active Fallout

Radio-active fallout through nuclear explosions is a serious modern problem. Nuclear explosions inject into the atmosphere considerable amounts of smaller particles called fission products. These contain unstable atoms, called radio-isotopes, which spontaneously break down emitting radiations and particles that are highly injurious to living tissues. The fission products finally reach the ground through rain, snow or wind. This is known as fall-out. The fall-out matter reaches man directly in drinking water, fruits and vegetables, or indirectly through animals, which eat contaminated feed or graze on contaminated pastures.
Many of the fission-produced radio-isotopes have half-lives (length of time that has to elapse before the amount of radioactivity measured has dropped to half the original value) of less than one day. Some have a half-life of a few days (8 days for $^{131}$ iodine) while others are radioactive for many years. The half-life of strontium$^{90}$ is 28 years and that of cesium$^{137}$ is 30 years. Even iodine, with a half-life of only 8-days, is hazardous for the normal functioning of thyroid. $^{90}$Strontium is considered to be the most hazardous radioactive isotope. It is closely related to calcium and the body treats both strontium and calcium in exactly the same way. $^{90}$Strontium induces bone cancer and leukaemia. $^{137}$Cesium passes through the human body quickly but it emits radiations which, through blood, reach all tissues and can be a potential genetic danger.

**Agricultural Contaminants**

Chemicals in the form of insecticides, fungicides, herbicides (in general biocides), growth promoting substances, and pollutants etc., are extensively used in large numbers in agricultural production. Without them much food would be lost. Commercial production of some crops would be impossible if chemicals are not used. It is estimated that 23 per cent of the commercial cabbage crop and 37 per cent of the potato crop would be lost if chemicals were not used. Small quantities of chemical residues often remain in such crops.

The residues of the pesticide DDT, has been observed in small amounts in soil, water, vegetables and animal tissues in all parts of the world. From these sources, the pesticide residues reach man. The widespread use of this chemical as an insecticide has contaminated even the air we breathe. The presence of pesticide and other residues in food is a serious international problem,
WHO has attempted to control the extent of contamination by prescribing the limits for the amount of many pesticides that may be present in foods. Some countries have banned the use of chemicals like DDT.

**Animal Food Additives**

They are also used as plant and animal additives. In some countries (particularly USA), about 80 per cent of animal feed is treated with small quantities of antibiotics for enhancing growth, improved feed utilization, and the checking of intestinal flora of animals. This has helped to produce less expensive meat and poultry. In all the cases where antibiotics have been used, residues may remain in meat. As already indicated, the presence of antibiotics in foods may result in the development of strains resistant to antibiotic drugs.

The synthetic female hormone, diethylstilbesteril (DES), is used on chicken, cattle, sheep as implants and as a daily additive to the feed. This helps the conversion of foodstuffs into meat more efficiently in such animals. On an average, the growth is one-fourth faster than in untreated animals; and the increase is more in muscle than fat. Residues of DES when present in food are potential cancer hazards.

Contamination of food in any way is bad. Just as in the case of food additives, food contamination must be considered in the light of any benefits that ensue. Use of pesticides is hazardous; but without pesticides much food would be lost. Some type of packing may result in contamination but the protection of food, requiring long-distance transport, from dirt and infection requires packing. Again, contamination of any type in very small
quantities may not be harmful, and in many cases the reported hazard has not been proved conclusively.

**Lecture: 2**

**SAFETY EVALUATION OF FOOD ADDITIVES**

Under Food additives Amendment two groups of ingredients are exempted from regulation.

**Group I:**

Prior sanctioned substances that FDA or USDA has determined safe for use in food prior to 1958 amendment.

   Eg: Sodium nitrate  
   Potassium nitrate

**Group II:**

It includes GRAS, all the substances approved by experts as safe based on their extensive history of use in food before 1958 or based on published scientific evidence.

   Eg: Salt, sugar, MSG

In 1969, president Nixon directed the FDA to update safety aspects of all GRAS substances on the basis of current scientific investigations.

In 1972 a committee from Federation of American societies for experimental biology reviewed the safety of all GRAS substances
on the basis of published and other available information. The committee placed all reviewed substances in five categories.

1. **Category I:**
   Includes all those additives whose GRAS status was reaffirmed. This means that the available information presented no evidence of toxic hazards of the substance in question. These substances are generally used according to GMP.

2. **Category II:**
   It includes those substances whose GRAS status was reaffirmed at current level of use. This means that the available information presented no evidence of toxic hazard at the level of current use and practice.

3. **Category III:**
   Substances whose safety is reaffirmed at the level of current use and practice. However certain uncertainties exist so that additional studies are required.

4. **Category IV:**
   Include those substances for which information is incomplete to “reaffirm safety”. This means evidence of toxicity has been reported, however the level and manner of current use the information is insufficient to determine the effect on public health.

5. **Category V:**
   Those substances for which no biological studies are available to judge their safety.
Safety of a Food Additive:

The limit should be established with due importance to following factors:

a. The estimated level of consumption of the food product by the consume world for which the additive is proposed.

b. Finding out minimum levels which would produce significant deviation from physiological behavior.

c. An adequate margin of safety to reduce any hazard to a minimum.

d. Legal control over the use of food additives. This can be accomplished only when a list of permitted additives exists with specified safe levels and toxic levels.

e. Stringent labeling on foods i.e., declaring the usage of additives in food and their quantities.

f. Employing trained food inspectors, food control laboratories and reliable analytical methods are of utmost important for regulation / control over usage of food additives.
### Some of the permitted GRAS Food Additives and Tolerances:

<table>
<thead>
<tr>
<th>Additive</th>
<th>Food used</th>
<th>Function</th>
<th>Tolerance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al,ca silicate</td>
<td>Table salt</td>
<td>Anticaking agent</td>
<td>2.0%</td>
</tr>
<tr>
<td>BHA</td>
<td>Various foods</td>
<td>Antioxidants</td>
<td>≤0.02%</td>
</tr>
<tr>
<td>BHT</td>
<td>Various foods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caffeine</td>
<td>Cola type beverages</td>
<td>Multipurpose</td>
<td>0.02%</td>
</tr>
<tr>
<td>Ca.silicate</td>
<td>Table salt</td>
<td>Anticaking</td>
<td>2.0%</td>
</tr>
<tr>
<td></td>
<td>Baking powder</td>
<td>Fumigants</td>
<td>5.0%</td>
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<tr>
<td></td>
<td>Cashew nuts</td>
<td>Flavoring agent</td>
<td></td>
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<tr>
<td>Ethylformate</td>
<td>Baked goods</td>
<td>Flavoring agent</td>
<td>0.05%</td>
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<tr>
<td></td>
<td>Puddings fillings</td>
<td></td>
<td>0.03%</td>
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<tr>
<td>Gelatin</td>
<td>General preservative</td>
<td>Antimicrobial</td>
<td>GMP</td>
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<tr>
<td>KMS</td>
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<tr>
<td>Sodium bisulphate</td>
<td>Various food</td>
<td>Antimicrobial</td>
<td>GMP</td>
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<tr>
<td>Sodium sulphite</td>
<td>Wines, fruit juices,</td>
<td>Antimicrobial</td>
<td>GMP</td>
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<tr>
<td></td>
<td>Dehydrated fruits</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Various foods</td>
<td>Sequestrants</td>
<td>0.15%</td>
</tr>
<tr>
<td>Stearylcitrate</td>
<td>Various fat</td>
<td></td>
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</tr>
</tbody>
</table>
Thiodipropionic acid containing foods Antioxidants 0.02%

Flow Diagram for International Acceptance of Food additives

Industry

Request for Data to be sent at Consideration of same time as request Food additive Food additive Data on specification

FAD (FS&T Branch) Rome

WHO (General)

due on use

Tolerances

Request for consideration Joint FAO/WHO program on FA Standards (codex Alimentarins)

Codex committee on FA, ministry of agriculture Mague, Netherlands.

Request for consideration

Commodity committees Of the codex Alimentarins.

Joint FAO/WHO Experts committee On FA

Tox. Eym specification Request for Consideration of data

Govt

Request for consideration Tolerances
<table>
<thead>
<tr>
<th>Additive</th>
<th>ADI Mg l kg 1 day</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. EDTA</td>
<td>2.5</td>
<td>Preservative, Sequestrants</td>
</tr>
<tr>
<td>2. BHA</td>
<td>0.5</td>
<td>Antioxidant</td>
</tr>
<tr>
<td>3. BHT</td>
<td>0.5</td>
<td>Antioxidant</td>
</tr>
<tr>
<td>4. Sodium nitrate</td>
<td>5.0</td>
<td>Curing agent, Colour fixation</td>
</tr>
<tr>
<td>5. Sodium nitrate</td>
<td>0.2</td>
<td>Curing agent, Colour fixation</td>
</tr>
<tr>
<td>6. Sod.stearyl fumarate</td>
<td></td>
<td>Stabilizing is non yeast leavened. Conditioning agent is yeast leavened.</td>
</tr>
<tr>
<td>7. Glycine</td>
<td>25</td>
<td>Stabilizer</td>
</tr>
<tr>
<td>8. Succinylated monoglyceride</td>
<td></td>
<td>Emulsifier, Dough conditioner</td>
</tr>
<tr>
<td>9. Polysorbate</td>
<td>25mg</td>
<td>Emulsifies</td>
</tr>
<tr>
<td>10. Propylene glycolalginate</td>
<td>25</td>
<td>Stabilizer, Emulsifier</td>
</tr>
</tbody>
</table>
Factors that affect toxicity or safety of toxicants:

Exogenous factors:

*Nature of the compound*: It depends on chemical structure and toxicity.

Eg: Ethanol \( \text{CH}_3\text{CH}_2\text{OH} \) 13.7 g/kg (ADI)

1,2- Ethane diol \( \text{HOCH}_2\text{CH}_2\text{OH} \) 6.1g/kg

- Dose of the compound
- Frequency of exposure
- Route of exposure
- Dietary factors: May delay or enhance or prevents absorption.

Endogenous factors:

- Binding of toxicants to plasma proteins and tissues.
- Excretory process: It is of two types
  1. Urinary excretion
  2. Biliary excretion

Dosage:

i) \( \text{LD}_{(50)} \):

Lethal Dose \( {}_{(50)} \) is used to “characterize the toxic potency of a compound”.
This is defined as that dose which produces a 50% mortality in a given test population. It is also used to indicate the magnitude of the toxicity.

Toxicity of a compound can also be used to expressed in terms of TD$_{50}$ (Tumor dose$_{50}$).

**ii) Virtually safe Dose:**
This is the exposure level which will produce only one tumor is 100 million persons.

**iii) No Effect Dose:** It shows safety of a compound. But identifying NED is quite difficult as most of the toxicants or chemicals often used show latency in human for even years.

**Lecture3**

**FOOD COLOURS/Color additives**
These include colour stabilizers, colour fixatives, colour retention agents etc. They consist of synthetic colours. Even though colours add nothing to the nutritive value of foods, without certain colours most consumers may not accept certain foods. Thus colours are frequently added to restore the natural ones lost in food processing or to give the preparations the natural colour we expect.

Originally many colour additives were natural pigments or dyes. For example, spinach juice or grass, marigold flower, and cochineal were used to obtain green, yellow and red colour respectively. This gave place to synthetic dyes obtained from coaltar. Synthetic colours generally excel in colouring power, colour uniformity, colour stability and cost. Further, in many cases, natural colouring materials do not exist for a desired hue. Carbonated beverages, gelatin dessert, candies and bakery goods are some foods that are coloured with coaltar dyes. As number of coaltar compounds have been shown to be potent
carcinogens, the use of coaltar dyes as food additives is restricted. Many countries have restricted the number of coaltar dyes for use in foods while some other countries have completely banned their use. Food colours also include some inorganic materials, such as iron oxide to give redness, and titanium dioxide to intensify whiteness.

A number of natural food colours extracted from seeds, flower, insects and foods are also used as food additives. One of the best known & most widespread red pigments is bixin, derived from the seed coat of Bixin orellana, the lipstick pod plant of south American origin. Bixin is not considered to be carcinogenic. The major use of this plant on a worldwide basis, however, is for the annatto dye, a yellow to red colouring material extracted from the orange red pulp of the seeds. Annatto has been used as colouring matter in butter, cheese, margarine and other foods. Another yellow both flavouring and colouring properties and has been used for colouring foods. Turmeric is a spice that gives the characteristic colour of curries and some meat products and salad dressings. A natural red colour, cochineal obtained by extraction from the female insect Coccus cacti, grape skin extract, and caramel, the brown colour obtained from burnt sugar are some natural colours that are used as food additives.

**Colours are used for following reasons**

1. Restore original appearance of the food which is lost during heat processing or storage.
2. Uniformity of colour as a result of natural variations.
3. To intensify colour as a result of natural variations.
4. To protect light-sensitive vitamins.
5. To impart attractive appearance to foods.
6. To preserve the identity by which foods are recognized.
7. To serve as visual indication of foods quality.
Safety Evaluation:

1. Prior to 1900, there was no regulation in the US on usage of food colours in processed foods.
2. With time colours proved to be toxic and their overuse often resulted in food poisoning.
3. National Academy of Science (NAS) cited certain cases leading to food poisoning due to HgS (vermilion) and Red lead (Pb₃O₄), copper arsenite and Lead chromate.
4. In the 20th century, food colours were under rigorous scrutiny for their technical suitability and toxicological properties.
5. U.S. Congress recognized the proliferation of colour additive usage as a threat to public health.
6. Then synthetic colours also known as Aniline dyes were manufactured from coal tar derivatives (from byproducts of petroleum industry).
7. USDA undertook the study of chemical and physiological properties of 100 coaltar dyes.
F & D Act of 1906: Listed seven dyes for use in foods.
   a. Amaranth
   b. Erythrosine
   c. Light green SF
   d. Orange I
   e. Ponceau 3R
   f. Indigosine
   g. Napthoyellow.

8. In 1938 Federal Food, Drug & Cosmetic Act which superceded the act of 1906, established mandatory certification. This act created three new categories of synthetic coaltar dyes.
I. D&C colours: Dyes and pigments considered safe in drugs and cosmetics when in contact with mucous membrane when ingested.

II. External D&C colours: Colours because of their oral toxicity were not certifiable for use in products intended for ingestion but safe for external use.

III. FD&C colours: Those certifiable for use in coloring foods, drugs and colors.

9. Colour Additives Amendment Act of 1960 defines a colour additive as any dye or pigment made or obtained from a vegetable or animal or mineral capable of colouring a food, drug or cosmetics or any part of the human body.

10. The law consists of two parts.
   I part: Delaney clause: To prohibit addition of any colourant which is carcinogenic.
   II part: Use of existing colours based on provisional listing pending completion of scientific investigation.

11. After 1982, to add any new colours to this list, the FDA requires results from toxicological studies.
   a. One sub chronic feeding (90 day) in a non-rodent species.
   b. Acute toxicity studies in rats.
   c. Chronic feeding studies in at least 2 species Eg: rats & mice (For 24-30 months)
   d. One teratology study
   e. One multigeneration reproduction.
   f. One mutagenicity test.

12. U.K. monitors food colours on the basis of a colour Index system. Certified colours are available as water soluble dyes or Insoluble dispersions lakes.
13. Except for lake FD & C Red No.40 all lakes are provisionally listed by FDA.
14. The soluble dyes readily dissolve in water and in certain polyhydric solvents such as propylene glycols.
15. FD&C dyes must contain a minimum of 85% pure dye, but commercially 90-93% pure dye content is seen.
16. If the sample complies with the specification, its certified & that batch is released for use.
17. The certification process ensures that every batch is chemically identical to the pigment used in animal feeding on which the approval is based.

**Colorants exempt for certification:**

C.A. Amendment Act (1960) : According to this act, colorants need not be certified prior to their sale but always under the surveillance of FDA to meet government regulations. Hence they are provisionally listed.
Food colours:

There are two types in Food colours. They are
i) Natural
ii) Artificial / synthetic

Synthetic food colours:

1. They are added to improve the appearance and eye appeal of preserve food products.
2. They have varied solubility. Soluble in water, oil, acids or alkaline.
3. Colours should be harmless, stable and their tint should be characteristic of the colour of the product.
4. Initially food colours, mostly permitted coal-tar dyes which were designated as synthetic colours by W.H.O (1958).

5. A part from International codex committee & FDA regulations, there are indigenous food laws such as F.P.O, PFA of govt of India which have laid down stringent regulations regarding usage of synthetic colours.

6. Red colour  \[ \begin{align*} &\text{Ponceau 3R} \\
&\text{Ponceau Xs} \\
&\text{Erythrosine} \rightarrow \text{xanthene} \\
&\text{Carmoisine} \rightarrow \text{Azo} \end{align*} \]  

Orange  \[ \begin{align*} &\text{Orange I} \\
&\text{Orange SS} \end{align*} \]  

Yellow  \[ \begin{align*} &\text{Tartrazine} \\
&\text{Sunset yellow} \end{align*} \]  

Green shade  \[ \begin{align*} &\text{Green F} \\
&\text{Pea Green H} \end{align*} \]  

**Certification of Food colour:**

- The safety of any new food colour is to be fully established by the user at his own cost to satisfy the Federal Authorities in USA.
- In Indian market most of the colours are imported especially from U.K called Edicol colours.
- Now even Indian labs (CFTRI, Defence Research labs) are working on the certification of food colours.

**Dyes & Lakes:**

Colour additives are available for use in food as either dyes or lake pigments.
Dyes
1. Dissolve in water
2. Insoluble in fat.
3. Manufactured as powders, granules, liquids.
4. Used in beverages, dry mix, confectionary.
5. Dyes also have side effects.

Lakes:
Combining dyes with salts to make insoluble
1. Lakes tint by dispersion i.e., oil dispersible
2. More stable than dyes
3. Ideal for colouring fat dense foods which lack moisture.

Some Natural food dyes:
1. Caramel (E150) - Caramelized sugar
2. Annatto (E160b) - Seeds of Achiote (Bixa orellano)
3. Green dye - Chlorella algae (chlorophyll E140)
4. Cochineal (E120) - Dactylopius coccus Red
5. Betalains - Beets (Red)
6. Turmeric (E100) - curcumin
7. Saffron (E160a)
8. Paprika (E160)
9. Elder berry juice - Sambucus nigra. (Black elder berry)

Synthetic food dyes:

<table>
<thead>
<tr>
<th>Colours</th>
<th>Chemical group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Tartrazine</td>
<td>pyrazolone</td>
</tr>
<tr>
<td>2. Sunset yellow</td>
<td>Monoazo</td>
</tr>
<tr>
<td>3. Erythrosine</td>
<td>Xanthene</td>
</tr>
<tr>
<td>4. Indigo carmine</td>
<td>Indigold</td>
</tr>
</tbody>
</table>
5. Fast green  
6. Brilliant blue  
7. Amaranth  
8. Allura red  
9. Black PN  
10. Fast red  
11. Patent blue  
12. Green S  
13. Ponceau 4R(Red)  

**Concept of Azo coupling:**

- Azo refer to ‘a’ = not zoa = to alive  
  - N=N- parent group  
  - H-N=N-H di imide group  

Azo dyes: Azo dyes have characteristic R-N = N-R bonding and are manufactured by Azo coupling.

An organic reaction between a diazonium compound and an aniline/ phenol/ benzene which produces a coloured Azo compound.

**Toxic Effects:**

FD & C Red No 1 : Monoazo :  
- Liver carcinogen (studied in Osborne mendelrats)  
  - At 0.5-5% of addition

FD & C Red No 2 :  
- Amaranth, Monoazo  
- Upto 5% level it is non toxic  
- But found to be embryotoxic in rats
FD & C Red NO 3:
- Non carcinogenic due to poor absorption
- Found to have toxic effects on thyroid and also disturb neuro transmitters which affect Fe absorption through membranes.

FD & C Red No 4:
- chronic follicular cystitis in liver
- Hemosiderotic focal lesions in liver
- Adrenal Atrophy

FD & C No 32:
- Growth retardation
- Liver damage

FD & C No 4:
- Non toxic

FD & C Blue No 1:
- 90% excreted

FD & C yellow No 5:
- Immune malfunction
- Urticaria
- Allergy
- Hyperkinesis
- Hypersensitivity
Lecture 4
Preservatives
Definition:
A preservative is defined as any substance which is capable of inhibiting, retarding or arresting the growth of microorganisms of any deterioration of food due to microorganisms, or of marking the evidence of any such deterioration.

The compounds used as preservatives are classified into two types. They are

1. Natural preservatives:

   Natural preservatives includes preservatives such as salts, sugar &, lemon etc.,

2. Chemical preservatives,

   Chemical preservatives are generally added after the foods are processed. The role of some preservatives is

   a) Sodium chloride :

   Salts stop the growth of microorganisms and interfere with the action of proteolytic enzymes. Salts also cause food dehydration by drawing out water from the tissue cells. Salt is employed to control microbial population in foods such as butter, cheese, cabbage, olives, cucumbers, meat, fish and bread. The amount of salt added determines the extent of protection afforded to the food. In the preservative action of NaCl, there is synergistic action with other intrinsic factors such as pH or extrinsic factors such as temperature, partial pressure of oxygen etc.,
b) Sugar:

Sugar acid in the preservation of products in which it is used. The high osmotic pressure of sugar creates conditions that are unfavourable for the growth and reproduction of most species of bacteria, yeasts and moulds. The preservative action of moderate strength of sugar can be improved if invertase is used to increase the concentration of glucose relative to sucrose. Foods in which sugars aid preservation include syrups and confectionary products, fondant fillings in chocolate, honey, jellies, marmalades, conserves and fruits such as dates, sultanas and currants.

3. Sulphur Dioxide:

It is used in the treatment of fruits and vegetables before & after dehydration to extend the storage life of fresh grapes, prevent the growth of undesirable microorganisms during wine making, and in the manufacture of fruit juices. Sulphur dioxide is also the most useful agent for the prevention of browning reactions in dried fruits. Most cut fruits are treated with sulphur dioxide to prevent enzymatic browning.

Forms in which sulphur dioxide is employed as a preservative include the gas (SO₂), the sodium and potassium bisulphites (NaHso₃ or KHSO₂ sulphites (Na₂SO₃ or K₂SO₃), and metabisulphite (Na₂S₂O₅ or K₂S₂O₅). At low pH values, the undissociated sulphurous acid predominates and inhibits the growth of yeasts and moulds.

4. Sorbic acid:
Sorbic acid (CH$_3$-CH = CH – CH = CH – COOH) and its sodium and potassium salts inhibit moulds and yeasts, in foods such as cheese, baked products, fruit juices, wines and pickles. The antimycotic action of sorbic acid is due to the inability of moulds to metabolize the conjugated unsaturated structure.

5. Acetic acid:

Acetic acid (CH$_3$COOH), in the form of vinegar, has been used to preserve pickled vegetables from antiquity. Acetates of sodium, potassium and calcium, are used in bread and other baked foods to prevent ropiness and the growth of moulds, but they do not interfere with yeasts. The acid is also used in foods, such as mayonnaise and pickles, primarily for flavor but these products also benefit from the concurrent anti-microbial action. The anti-microbial activity of acetic acid increases as the pH decreases.

6. Propionic acid:

Propionic acid (CH$_3$CH$_2$COOH) and its sodium and calcium salts exert antimicrobial activity against moulds and some bacteria. The acid finds extensive use in bakery field, where it not only inhibits moulds effectively but is also active against the ropy bread organism Bacillus mesentericus. The toxicity of propionic acid to moulds and certain bacteria is related to the inability of the organisms to metabolize the three-carbon unit.

7. Benzoic acid:

Benzoic acid is widely used as an antimicrobial agent. Its sodium salt is more soluble in water than the free acid and hence it is generally used. The acid is most active against yeasts and bacteria and least active against moulds. It exhibits optimum
activity in the $p^H$ range 2.5 – 4.0, and thus is well suited for use in acid foods, such as fruit juices, carbonated beverages, pickles & sauerkraut.

8. Parabens:

These are alkyl esters of p-hydroxy benzoic acid. The methyl, ethyl, propyl and heptyl esters are generally used. These are effective inhibitors of moulds and yeasts, but are relatively ineffective against bacteria. They are active at $p^H$ 7 and higher and have little effect on flavor.

9. Epoxides:

Epoxides are cyclic ethers that destroy all forms of microorganisms including spores and even viruses. The epoxides used as preservatives are ethylene oxide and propylene oxide. The epoxides are used in gaseous form and after adequate exposure, the residual epoxide is removed by flushing & evacuation. Their use is limited to dry items, such as nuts and spices.

Lecture 5
Antioxidants and chelating agents

Antioxidants:

An antioxidant is a substance added to fats and fat containing substances to retard oxidation and thereby prolong their wholesomeness, palatability and sometimes shelf life.

According to Rule 58 of PFA rules (1955), an antioxidant has been defined as a substance which when added to food retards or prevents oxidative deterioration of food.
Generally oxidative rancidity occurs in oils having a high degree of unsaturation. Fats tend to spoil due to rancidity. Rancidity is of 2 types.

1. Hydrolytic rancidity
2. Oxidative rancidity

In hydrolytic rancidity the triglyceride reacts with water and for each molecule of water involved one molecule of fatty acid is released.

\[
\text{Triglyceride} + 3\text{H}_2\text{O} \rightarrow \text{Glycerol} + 3\text{fatty acid.}
\]

Heat / lipase

Eg: Butter becomes rancid due to the release of butyric acid.

Oxidative rancidity is catalyzed by temperature, very low humidities, UV, presence of trace minerals (cu, Fe & co) & degree of unsaturation. Oxygen susceptibility increases with the way the unsaturated fatty acids are distributed in the glycerol moiety.

Natural oils & fats are less prone to oxidation due to the presence of antioxidants like tocopherols. Refined oils are prone to rancidity.

Oxidation forms peroxides and hydroperoxides followed by aldehydes, ketones & acids which are responsible for off odours and off flavours associated with the rancid fats.

Process of oxidative rancidification:

\[
i) \quad \text{H-C-C = C-C-H + a quantum of energy} \quad \rightarrow \quad \text{H-C-C = C-C-H+H} \quad \text{labile}
\]

Unsaturated fatty acids freeradical

hydrogen
A free radical formed marks the beginning of a self perpetuating chain reaction leading to the formation of hydroperoxides. Hydroperoxide is very unstable decomposing into compounds of shorter carbon chains. They include fatty acids, aldehydes & ketones which are volatile and which contribute to the unpleasant odour to rancid fats. Oxidation may be catalysed by the enzyme lipoxygenase as well as heat, light & certain metals like Cu, Fe. These are called prooxidants, as they promote oxidation.

Eg: Fe from Hb catalyses rancidity in cooked meats.

Oxidation of linoleic acid forms an aldehyde called 6-Nonenal which is responsible for the off odour during the process of flavor reversion. Autocatalytic oxidative rancidity occurs in fats due to enzyme lipoxygenase.
Natural antioxidants:

The natural antioxidants present in foods inhibit formation of anti carcinogenic Nitrosamines.

Vitamin c or Ascorbic acid (fruits and vegetables)
Vitamin E or tocopherols (grains, edible oils)
Catechins (Tea)

For e.g., Enzymatic browning in cut fruits and vegetables is due to enzymatic oxidation of phenolic substances. Antioxidant like Vitamin C can prevent this browning. Citric acid & phosphoric acid increase the effectiveness of ascorbic acid in this process.

Synthetic antioxidants:
The most common synthetic antioxidants are
BHA – Butylated Hydroxy Anisole
BHT – Butylated Hydroxy toluene
Propyl gallate (PG)
Tertiary butyl hydroquinone (TBHQ)
Thiodipropionic acid
Dilauryl thio dipropionate

The joint FAO/WHO expert committee on food additives has suggested ADI for BHA as 0.05 mg /1kg body wt and BHT as 0.03 mg/ 1kg body weight.

Acidic compounds / chelating agents are considered as synergists as they chelate or scavenge the free radicals & pro oxidant molecules thereby enhancing the activity of antioxidants.

Antioxidant molecules generally replace UFA as a source of labile hydrogen to unite with a free radical to form an activated peroxide. In
this process the molecule of antioxidants is oxidized instead of another fatty acid. Thus antioxidants prevent oxidative chain reaction.

\[
\text{AH} + \text{ROO}^0 \longrightarrow \text{ROOH} + \text{A}^0
\]

\[
\text{RH} + \text{A}^0 \longrightarrow \text{AH} + \text{R}^0 \quad \text{Incapable of initiating the chain}
\]

\[
\text{AH} + \text{ROO}^0 \longrightarrow (\text{ROO}^0\text{AH}) \quad \text{Non-radical product}
\]

\[
\text{A}^0 + \text{R}^0/\text{ROO}^0 \longrightarrow \text{RA} + \text{ROOA}
\]

\(\text{R}^0 \) – free radical (any species capable of independent existence that contains one or more unpaired e)

\(\text{AH} \) – antioxidant

**Propyl gallate:**

\[
\text{COOCH}_2\text{CH}_2\text{CH}_3
\]

- Synergic in function with acids, BHA & BHT
- Used as an antioxidant in foods, fats, oils, ethers, emulsions, waxes & transformer oils.
BHA (Butylated hydroxy Anisole):

\[
\begin{align*}
\text{OH} & \quad \text{C(CH}_3\text{)}_3 \\
\text{O CH}_3 & 
\end{align*}
\]

- Synergic in function with PG, HQ, lecithin etc.,
- Usually used in meat industry, AIMF – 72 (Anti oxidant formulation)
  
* 20% BHA
* 6% Propyl gallate
* 4% citric acid is propylene glycol

BHT (Butylated Hydroxy Toulene)

\[
\begin{align*}
\text{OH} & \quad \text{C(CH}_3\text{)}_3 \\
(CH}_3\text{)}_3 & \quad \text{C(CH}_3\text{)}_3 \\
\text{CH}_3 & 
\end{align*}
\]

- More soluble in food oils and fats than BHA.
**Toxic effects:**

- Long term use of antioxidants above the levels of ADI can be carcinogenic.
- PG & BHA/BHT can be carcinogenic, proved in rats.
- In case of BHA, it is rapidly absorbed in GIT, rapidly metabolized & completely excreted in urine
- Major metabolites of BHA are gluconamides, ether sulphates & free phenols.
- Harmful effects:
  - Impaired growth
  - Impaired enzyme activity
  - Increased excretion of Na & K
  - Liver enlargement
  - Proliferation of ER
  - Above 2% can cause Neoplastic lesion & cancers.

**Chelating Agents:**

Chelation means a chemical mechanism through which compounds in whom a central metallic ion is joined by bonds to 2 or more non-metallic atoms of the same molecule so that one or more heterocyclic rings are formed with the central ion as part of each ring.

**For Eg:**

Citric acid which plays a dual role of an acid as well as of a base because, it has displaceable hydrogen atoms and a pair of unshared electrons. Alpha acids like citric acid & tartaric acid are better to hold tripositive ions in solution at $p^H7$. 
According to Walton(1966), ability to form a neutral chelated compound with the metal ion in an organic molecule must have a dual character i.e., a molecule must be acidic which means it should have displaceable H\(^+\) ion/atom and on the other hand it must also be basic which means it must have a pair of unshared electrons. OH group is a universal complex former by virtue of its dipole movement and unshared electrons.

Example: Citric acid, Tartaric acid, Ca and Na Ethylene diamine tetraacetate, adipic acid (acidulant)

Chelators regenerate the primary antioxidant according to the reaction

\[
\text{SH} + \text{A}^0 \rightarrow \text{AH} + \text{S}^0
\]

e.g., Ascorbic acid, Ascorbyl Palmitate

\[
2\text{AA} + \text{O}_2 \rightarrow 2\text{dehydro} - \text{AA} + 2\text{H}_2\text{O}
\]

\[
2\text{AP} + \text{O}_2 \rightarrow 2\text{dehydro} - \text{AP} + 2\text{H}_2\text{O}
\]

Sequestering agents according to PFA Rule 70, are substances which prevent adverse effects of metals catalyzing the oxidative break down of foods forming chelates thus inhibiting discoloration, off taste and rancidity which remain active in alkali solutions.

Recommended usage levels for citric acid typically vary between 0.1 & 0.3% with appropriate antioxidant at levels ranging between 100ppm & 200ppm.
Citric acid exerts its inhibitory action on Polyphenol oxidase by lowering the $\text{pH}$ as well as chelating the ‘cu’ at active site of the enzyme.

**Other chelating agents:**

1. EDTA & Polyphosphate: Canned sea foods. The magnesium in sea foods which may react with $(\text{NH}_4)_3 \text{PO}_4$ to form glossy crystals (struvite). Fe, Cu, & zinc containing sea foods react with sulphides which may lead to discolouration.
2. Polysaccharides like Xylan sulfate, Carrageenan amylose sulfate & pectin are used as chelators and browning inhibitors in both apple juice & apples.
3. Phosphoric acid

**Toxic Effects:**

- Most of the chelating agents are inorganic & hence disturb the mineral balance in the body.
- Phosphates disturb and damage kidney, growth reduction & heart damage.
- Vinegar can cause renal failure, ulcers in gut mucosa and, reduction in clotting efficiency.

**Lecture 6**

**Surface Active Agents**

Food products generally are multiphase systems in which solids, liquids and air are finely distributed during manufacture to give the finished product the desired structure & shelf life.

As many of these phases for e.g., oil & water are not miscible substances. Hence it is required to facilitate phase distribution during manufacture to ensure stability and prevent separation during storage.
Surface active agents exhibit a phenomenon called “surface activity” because of which miscibility of otherwise immiscible components is possible.

Surface active agents/ Tensides are generally used in food industry when a decrease in surface tension is required.

Surface active agents

- Natural
  - Neutral
    - Glyco lipids
  - Ionic
    - Bile salts
    - Phospho lipids
    - Inositol phosphate

- Synthetic
  - Ionic
    - Soaps(esters)
    - Dioctyl sodium
    - Sulpho succinate
  - Non ionic/neutral
    - propylene glycerol monoester
    - sorbitol esters
    - poly glycerol esters etc.

A tenside with a relatively strong lipophilic group and weak hydrophilic group is mainly soluble in oil and preferentially stabilizes a water in oil emulsion & vice versa. This fact led to the development of a standard with which the relative strength or activity of the hydrophilic & lipophilic groups of emulsifiers can be evaluated. It is called “Hydrophilic Lipophilic balance” (HLB). It can be calculated from chromatography behaviour & dielectric constants of surfactants. For fatty acid esters:

\[
HLB = 20 \left(1 - \frac{SV}{AV}\right)
\]

\[
SV \quad \text{--- Saponification value}
\]
**Acid value**

\[ \text{AV} \text{ --- Acid value} \]

\[ \text{Or HLB} = \sum (\text{Hydrophilic Group number}) - \sum (\text{hydrophobic group number}) + 7 \]

**Synthetic Emulsifiers:**

There are about 1,50,000 – 2,00,000 of emulsifiers of which mono, diglycerides & their derivatives account for the largest part i.e., about 75%.

e.g: Di acetyl tartaric acid ester of monoglyceride (DATEM)
- Sorbitol monostearate
- Sorbitol tristearate
- Stearyl monoglyceride
- Sodium oleate
- Potassium oleate

**Properties of surface active agents:**

*Wetting (In rehydration of powders containing fats surface active agents increase the penetration of water)*

*Dispersion or emulsifying action:
Generally dispersion system involves liquids, solids & gases.

<table>
<thead>
<tr>
<th>Dispersion systems</th>
<th>Inner phase</th>
<th>Outer phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Emulsion</td>
<td>liquid</td>
<td>liquids</td>
</tr>
<tr>
<td>b. Foaming</td>
<td>Gaseous</td>
<td>liquid</td>
</tr>
<tr>
<td>c. Aerosol</td>
<td>liquid or solid</td>
<td>Gaseous</td>
</tr>
<tr>
<td>d. Suspension</td>
<td>solid</td>
<td>liquid.</td>
</tr>
</tbody>
</table>

*Emulsifying action*
*Foams induce stability  
*Dispersion of solids or liquids in gases by Aerosols.  
*Solid is dispersed in liquid by suspension.  
  Eg: Chocolate powder in milk  
*Lubrication and reduces stickiness.  
*Complexing: Surface active agents like mono & diglycerides react with amylase & prevent retro gradation of amylase. Hence addition of mono & diglycerides to bread dough before baking can prevent retro gradation of amylase.  
*Shortening: Shortenings are used in bakery & confectionary (2.5% mono glycerides ) is used.  

**Emulsions & Emulsifiers:**

Emulsions are dispersed systems, usually comprises of two immiscible liquids, where the outer phase consists of water and the inner of oil, it is considered as “oil in water” (O/W) type of emulsion. When this is reversed i.e., water is dispersed in oil, a w/o emulsion exists.  

eg., Milk (O/W)  
  Butter (W/O)  

Visual appearance of an emulsion depends on the droplet diameter. If the diameter is in the range of 0.15 - 100µm the emulsion appears milky – turbid. In comparison micro emulsions of diameter 0.015-0.15 µm are transparent and considerably more stable because the sedimentation rate depends on the droplet diameter.  

Emulsifiers are substances because of their molecular structure they are deposited at the phase (inter phase) and help to stabilize the phases. Each emulsifier can disperse a limited amount of an inner phase, i.e., it has a fixed capacity. When the limit is reached further addition of outer phase breaks down the emulsion.
**Mechanism of action of Emulsifiers:**
Emulsions are made and stabilized with the aid of a suitable tenside (surfactant). The emulsifier molecule has at least one group with polar affinity i.e., hydrophilic soluble in H\textsubscript{2}O and one group with lipophilic or hydrophobic nature which is soluble in fat. Hydrophobic group is usually a long chain or alkyl residue or fatty acids while hydrophilic part of the molecule consists of a dissociable group or number of hydroxyl or polyglucoether groups. Through the presence of hydrophilic & lipophilic group in the molecule, emulsifiers interact with water & with fats or oils.

The emulsifier is oriented at the phase interface with the hydrophilic component going towards the water and the lipophilic component towards oil. This causes a film to be formed which reduces surface tension. In an immiscible system such as oil or water the emulsifier is located on the interface, where it decreases interfacial tension. It facilitates a fine distribution of one phase within the other. The emulsifiers also prevent droplets once formed from aggregating & coalescing i.e., merging into a single large drop.

**CMC (Critical Micelle Concentration)**

**Or lyotrophic Mesomorphism**

- CMC is a function of emulsifier concentration above which the emulsifier aggregates, reversibly to give spherical micelle, changing surface tension slightly.
- CMC is a characteristic value of the emulsifiers which decreases as the hydrophobic part of the molecule increases. It is generally influenced by temperature, P\textsuperscript{H} & electrolytic imbalance.
- The temperature at which the solubility of an emulsifier reaches the CMC is called critical micelle temperature (T\textsubscript{c})
- Crystals, micelles & the dissolved emulsifiers are in equilibrium at the T\textsubscript{c} and an emulsifier cannot form micelles below the T\textsubscript{c}.
Emulsifiers are lyotropic mesomorphs depending on water content & temperature.

**Lecture 7**

**Substitutes for Fat**

**Definition:**
Substances which are capable of serving the different functions of fat at the same time giving less energy compared to fat. Fat substitutes are of two types:

1. Natural (Fat mimetics)
2. Synthetic

Fat mimetics are of two types

1. Microparticulated proteins
2. Carbohydrates

**Microparticulated proteins:**
They are used in milk products like desserts & Ice creams. Proteins of (8µm or more) diameter are generally sandy & those in the range of 3-8 µm are powdery & 0.1 - 3µm are creamy and 0.1 µm are watery. Microparticulation of protein concentrates where the size is reduced to 0.1 -3µm can cause melt-in-mouth feeling produced by fat. In this process generally ovalbumin, casein and whey protein are exposed to varying pressures and temperatures where they are ground by shear forces. Immediately they are cooled rapidly to 4-10°C. 3g of swollen substitute can replace 3 gm of fat (1g+2g water) but provides only 4 k cal

**Carbohydrates:**
Polymeric carbohydrates are generally preferred as fat substitutes. For e.g., from cornstarch non-sweet oligosaccharides and maltodextrins which dissolve completely in water are obtained. When this solution is cooked, a gel is formed which has the texture of edible oil. It can partially replace fats. Energy gain is 2 k cal/g. It can replace fat in margarine.
Polymeric carbohydrates are non-digestible which on microbial degradation produces short chain acids. These acids are absorbed & release energy. The carbohydrate based fat substitutes include resistant starches formed during starch retrogradation, fructose polymers, pectin & carboxy methyl cellulose etc.,

**Synthetic fat substitutes:**

Energetically inefficient fat substitutes can basically be made by

- Replacement of glycerol with other alcohols.
- Replacement of usual fatty acids with branched, polybasic or long chain carboxylic acids.
- Introduction of ester bonds.
- Use of ether instead of ester bonds.

**Carbohydrate polyesters:**

Mono, Oligo and polysaccharides yield fat like products when esterified with fatty acids e.g., Olestra -6-8 OH groups are esterified with fatty acids (18-12 carbon number). This is tasteless and thermally stable and hence can be strongly heated as an edible fat during baking and frying.

**Retro fats:**

These are esters of polybasic acids (like malonic acid, citric acid propane, 1,2,3 –tri carboxylic acid, butane 1,2,3,4 – tetra carboxylic acid) with long chain alcohols.
Lecture 8

Stabilizers & Thickeners

These are food additives which are used to improve and stabilize the viscosity and consistency of foods.

Functions:

- Improve and stabilize consistency
- Inhibit crystallization
- Stabilize emulsions & foams
- Reduce stickiness of Icings
- Encapsulate flavours.

Eg Polysaccharides  Gum Arabic

Guar gum

Carrageenan

Sodium alginic acid

Starch

Carboxy methyl cellulose.

The only non protein based material used as a thickener – gelatin.

Mechanism:

They readily swell in hot or even cold water & help thicken food. They are hydrophilic and are dispersed in solution as colloid.

Algin and Alginates in foods (Algin is sodium salt of alginic acid also called as sodium poly mannuronate):
They are extensively used in the preparation of ice creams, in the production of dairy products, such as whipped creams, milk powders, milk shakes, processed cheese. They prevent the formation of ice crystals during the process of freezing and produce uniform viscosity and whipping ability. In sugar grained confections, they modify the crystal size without affecting flavor. In beverages such as rose wines they are used for clarifying and purifying and also as foam stabilizers. Alginate gels are used for deep freezing of fish.

**Agar**: Also known as Agar-agar. A polysaccharide complex extracted from agarocytes of algae of the family Rhodophyceae. It can be separated into a gelling fraction agarose, and a sulphated non-gelling fraction –agaropeptin. Generally used in pie fillings, custards, Jellies for thickening purpose.

**Pectin**: It is a polysaccharide substance present in cell walls in all plant tissues which functions as an intercellular cementing material. One of the richest sources of pectin is lemon or orange rind which contains about 30% of this polysaccharide. Almost completely soluble in water it forms a viscous solution containing negatively charged very much hydrated particles. It is widely used as a setting, jellying and solidifying agent in jam, jellies, and marmalades and as stabilizing agent in beverages.

**Gelatin**: Gelatin is obtained from collagen by hydrolytic action. Gelatin is used as a thickener and stabilizing agent in ice creams, yoghurts and pie fillings.

**Carboxy methyl cellulose**: It is modified cellulose and the principal compound is carboxy methyl D-glucose.
Lecture 9:

Leavening Agents

Leavening agents produce light fluffy baked foods. Originally, yeast was used most exclusively to leaven baked products. It is still an important leavening agent in bread making.

These are of two types

1. Natural : Yeast activity on sugars leading to CO₂ generation.
2. Synthetic : Baking powders or chemical leavening agents

   Baking powders have two components.
   i) Baking soda E.g. NaHCO₃, NH₄HCO₃
   ii) Acid ingredients E.g: Tartaric acid

   Mono calcium phosphate
   Sodium aluminium sulphate

→ In the market baking powders are named after their acid component like tartarate powders, phosphate powders etc.,

   NaHCO₃ + HX --→ Na x + H₂O + CO₂
   Baking soda Acid

→ Baking soda is usually added to an extent of 28-30%
→ An inert filler like corn starch is also added which acts as buffer avoiding the reaction between soda and the acid.
→ Baking powder yields 12-14% CO₂
→ Tartarate powders are fast acting & hence lot of CO₂ is lost before baking.

*Double acting powders: They are slow in action. The powder contains two acid reacting ingredients of which one is a slow one, generally the
ingredient being mono calcium phosphate & sodium aluminium phosphate.

\[2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2\]

\[2\text{NaHCO}_3 + \text{COOH} \rightarrow \text{COONa} + 2\text{H}_2\text{O} + 2\text{CO}_2\]

\[
\begin{align*}
\text{CHOH} & \quad \text{CHOH} \\
\text{CHOH} & \quad \text{CHOH} \\
\text{CHOH} & \quad \text{COONa}
\end{align*}
\]

\[8\text{NaHCO}_3 + 3\text{CaH}_4(\text{PO}_4)_2 \rightarrow \text{Ca}_3(\text{Po}_4)_2 + 2\text{Na}_2\text{HPO}_4 + 8\text{H}_2\text{O} + 8\text{CO}_2\]

\[6\text{NaHCO}_3 + 2\text{Na}_2\text{Al(SO}_4)_2 \rightarrow 2\text{Al(OH)}_3 + 4\text{Na}_2\text{SO}_4 + 6\text{CO}_2\]

**Yeast:**

Unicellular microorganism which is active at pH 4 and temperature 30\(^{0}\)c

It acts on sucrose releasing glucose and fructose which in turn get broken down into alcohol and carbon dioxide

Invertase

\[
\begin{align*}
\text{Sucrose} & \quad \rightarrow \quad \text{Glucose} + \text{Fructose} \\
2\text{C}_6\text{H}_{12}\text{O}_6 & \quad \rightarrow \quad 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2
\end{align*}
\]

(GLucose)

**Lecture 10**

**Bleaching and Maturing Agents**

Bleaching and maturing agents are flour improvers widely used in Bakery Industry.
* Purpose of the above bleaching and maturing agents is to mature & bleach the flours.
* Freshly milled flour has a yellowish tint and yields weak dough that produces poor bread. Both the colour & baking properties improve by storing the flour for several methods before making bread.
* During storage atmospheric oxygen oxidizes the carotenoid pigments responsible for the colour of the flour converting them to colorless compounds.
* They also oxidize some of the proteins which form the dough to give the dough increased strength & elasticity.
* As this is a time consuming process flour improvers can be used to bring about the changes.

Additives /chemical agents added as flour additives are oxidizing agents which may participate in bleaching only, in both bleaching and dough improvement or dough improvement only. Both the categories of substances are oxidizing agents.

**Bleaching agents:** Examples are Benzoyl peroxide, Cl₂, Clo₂, NaCl, No₂ and N₂O₄ etc, Azo dicarbonamide & Ascorbic acid.

Benzoyl peroxide is used for only bleaching action \((C₆H₅CO)₂O₂\) and relatively slow in its action.

**Both for bleaching & improving:**

Oxidizing action of Cl₂, Clo₂, Nitrosyl chloride and Nitrogen di tetra oxides.
Additives used only for maturation/ Dough improvement:

KBro₃(Potassium Bromate), KIO₃, Ca(Io₃)₂ & Calcium peroxides.

- The gaseous agents used for bleaching and improvement act immediately on contact with flour.
- Oxidizing agents used for dough improvement remain inactive until yeast fermentation lowers the P_H of the dough sufficiently to activate them. As a result of late action, they cause increase in loaf volume, increased loaf symmetry and improved crumb & texture characteristics.
- The oxidizing agents oxidize sulphhydryl groups (-SH) in the proteins of gluten to yield an increased number of intermolecular disulphide bonds (-S-S) resulting in tougher, drier & more extensible dough that gives rise to improved characteristics.
- Ascorbic acid is the most preferred improver for a specific bread making process which involves intense mechanical working of the dough. Ascorbic acid acts as antioxidant, Nutritive additive, and Dough improver.
- These kinds of additives are generally added to adjust the flour characteristics to match the baking process.

Eg: In case of ascorbic acid 40mg/kg of flour has a best strengthening effect on dough.

- In dough making, the ascorbic acid added to the flour oxidizes rapidly to DHA’s (Dehydro Ascorbic Acid). At the same time Stereo-isomers of Ascorbic acid are formed.
Eg: L-threo-Asc (vit c)

D-threo-Asc

D-erythro-Asc (Iso ascorbic acid)

L-erythro-Asc

L-threo –Asc has the highest degree of sough strengthening effect & D-threo- Asc is ineffective.

\[ \text{Asc} + \text{O}_2 \rightarrow \text{DH Asc} \quad \text{(a)} \]

Glutathione oxidase

GSH (Glutathione) is oxidized to \[ \text{GSSG} \quad \text{(b)} \]

Dehydrogenase

(oxidized Glutathione)

In this process DHASc can be reconverted to Asc. Hence small quantities will serve the function. GSH dehydrogenase found in flour plays an important role in dough improvement when Ascorbic acid is added.

The oxidized glutathione can undergo an SH/SS exchange with gluten proteins in the presence of Ascorbic acid. GSH is incorporated into gluten proteins as terminator of polymerization via intermediate GSSG.

\[ \text{GSSG} + \text{PSH} \rightarrow \text{PSSG} + \text{GSH} \quad \text{©} \]

Interconversion of SH --\( \rightarrow \) SS

\[ \text{GSH} + \text{PSSP} \rightarrow \text{PSSG} + \text{PSH} \]

Gluten Protein
GSH is also oxidized immediately. During this stage a+b+c stops when all the GSH is present as GSSG or incorporated into gluten proteins. Consequently GSH is largely withdrawn from the dough before it can depolymerize the gluten proteins by SH/SS interchange. If it is not withdrawn--

\[
\begin{align*}
PSSP + GSH & \rightarrow PSSG + PSH \quad (d) \\
CSSC + GSH & \rightarrow CSH + GSSC \quad (e) \\
PSSP + CSH & \rightarrow PSSC + PSH \quad (f) \\
CSSC + PSH & \rightarrow PSSC + CSH \quad (g)
\end{align*}
\]

This reaction results in softening of the dough because GSH cleaves intermolecular disulfide bonds of gluten. GSH reacts with cysteine present in flour and increases cysteine (SSH) which can depolymerize gluten strands & proteins. Cysteine:

It is used in hydrochloride form which softens gluten due to SH/SS interchange with in the glutenin fraction. The resistance to extension of the dough decreases and extensibility increases. It increases dough development time and dough stability & a good baking volume.

**Bromate, Azo dicarbonamide**:

- Prevents excessive softening of gluten during dough mixing.
- This reaction involves oxidation of endogenous glutathione to its disulfide.
- This additive can link gluten protein by the formation of intermolecular disulfide bonds. During baking bromates are
completely reduced to bromides with no bromination of flour constituents.

Azo dicarbonamides:
- It improves the properties of wheat gluten but decreases the energy input in dough mixing.
- Lipoxygenase exhausted from soy flour increases mixing tolerance, improves dough rheology & increase bread volume.

Lecture 11
Starch Modifiers
Definition:
Starch properties and those of amylose and amylopectin can be improved or tailored by physical and chemical methods to fit or adjust the properties to a particular application of food products.

Types of Modified starches:
1. Mechanically damaged starches:
When starch granules are damaged by grinding or by application of pressure at various water contents the amorphous portion is increased resulting in increased dispersibility & swellability in cold water.
   * Decrease in gel temperature by 5-10°C
   * Increase is enzymatic vulnerability

2. Extruded starches: Starches subjected to extrusion.
   * Increases dispersibility (x-ray diffraction changes from ‘V’ pattern to E pattern) at high temperature decreases cooling.
   * Extruded have a lower viscosity.

3. Dextrinized starch:
   * Heating of starch to 100-200°C with acidic or basic agents causes degradation of starch.
* Powders are sticky, turbid solutions which can be used as adhesives in sweets and fat substitutes.

4. **Pregelatinized starch**:
   * Heating of starch suspensions followed by drying provides products swellable in cold water & forms gels on heating.
   * Mostly used in instant foods, pudding and weaning foods.

5. **Thin-Boiling starch**:
   * Partial acidic hydrolysis yields a starch product which is not very soluble in cold water but readily soluble in boiling water.
   * Lower viscosity and remains fluid after cooling. Retrogradation is slow.
   * These starches are utilized as thickeners and as protective films.

6. **Starch Esters**:
   * When 30-40% starch suspension is reacted with ethylene oxide in the presence of hydroxides of alkali or alkali earth metals (P ≈ 11-13) starch ethers are formed.
   * Used in refrigerated foods (pie filling)
   * These products swell instantly in cold water
     Starch +Mono chloroacetic acid \( \rightarrow \) Carboxy methyl starch
   * Dispersions at 1-3% give ointment and at 3-4% gives gel like consistency.

7. **Starch Esters**:
    Starch mono phosphate ester is produced by dry heating of starch with alkaline orthophosphate or alkaline tripolyphosphate at 120-175\(^0\)c
* Thickener and also a stabilizer in bakery foods, heat-sterilized canned foods and microencapsulation of flavours.

8. Cross linked starches:

* Starch +bi/poly functional reagents such as sodium tri meta phosphate, phosphorus oxy chloride, Epichlorhydrin etc.,
* Increase in gelatinization temperature is directly proportional to extent of cross linking.
* “starch stability” at high temperature & P\(^H\) is achieved.

9. Oxidised starches:

* Starch hydrolysis & Oxidation occur when an aqueous starch suspensions are treated with sodium hypochlorite at a temperature below starch gelatinization temperature.
* Used as a “Lower viscosity filler” and these starches show no retrogradation and no gelation.

Lecture 12

Acids, Bases and Buffers

Acids, bases and salts dissociate in aqueous solutions into positively charged and negatively charged atoms or groups of atoms called ions. This process is known as ionization. In an electric field, the positively charged ions move towards the negative electrode (cathode) and the negatively charged particles, towards the positive electrode (anode). The current is carried across the solution by ions and not by electrons as in the case of metals. Liquids, in which this type of electric conductance takes place, are known as electrolytes.

According to the classical definition (Arrhenius), a substance which on ionization in aqueous solution yields hydrogen ions (H\(^+\), proton) is
an acid and one that yields hydroxyl ions (OH) is a base. As there is a strong affinity between hydrogen ions and water molecules, they produce hydronium ions (H^+ + H_2O → H_3O^+). A substance which undergoes complete ionization (100 percent) is a strong acid or base, while that which undergoes partial ionization (i.e., considerably less than 10 per cent) is a weak acid or base.

\[
\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-
\]

Strong Hydronium Chloride ion

\[
\text{CH}_3\text{. COOH} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CH}_3\text{. COO}^-
\]

Weak acid Acetate ion

\[
\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}^+ + \text{OH}^-
\]

Strong base Sodium ion Hydroxyl ion

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-
\]

Weak base Ammonium ion

Water is a very weak conductor of electricity which shows that it is ionized to a very small extent. To conduct electric current, however tiny the conduction is, water must dissociate to a very small extent forming hydrogen or hydronium and hydroxyl ions. For example, hydrogen chloride (HCl) dissolved in the non-aqueous solvent, benzene, gives no evidence of the presence of ions, yet it shows the reactions of acids. Again, liquid ammonia ionizes, \( \text{NH}_3 \rightarrow \text{H}^+ + \text{NH}_2^- \); the
amide ion is a strong base akin to the OH\(^-\) ion. To account for these, Bronsted and Lowry gave a more general definition of acids and bases. According to them, an acid is any substance that donates a proton to another substance and a base is any substance that can accept a proton.

From this point of view, in the ionization of acetic acid

\[
\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{ . COO}^- \\
\text{Acid}_1 \quad \text{Base}_1 \quad \text{Acid}_2 \quad \text{Base}_2
\]

\( \text{CH}_3\text{COOH} \) is an acid for it gives up a proton. Water is a base because it accepts a proton. In this reverse reaction, \( \text{CH}_3\text{ . COO}^- \) is a potential proton acceptor, and hence the ion is a base. \( \text{H}_3\text{O}^+ \) ion is an acid, because it is now a potential proton donor. \( \text{Acid}_2 \) resulting from base is said to be the acid conjugate of \( \text{base}_1 \). Similarly, \( \text{base}_2 \) is the conjugate of \( \text{acid}_1 \). Thus, most substances called acids or bases according to the classical definition are also acids and bases when the Bronsted-Lowry definition is used. The new definitions are much broader and can be applied to non-aqueous systems. The strength of an acid depends upon the percentage of its ionization. An acid that is 50 per cent ionized will yield a greater amount of \( \text{H}^+ \) than one that is 5 per cent ionized. At constant temperature, the extent of ionization is a constant value and is characteristic of an acid.

The acids in food processing are used to decrease the \( \text{P}^{\text{H}} \) according to the processing requirements. The common acidulants used are citric acid, lactic acid, acetic acid, tartaric acid etc., Tartaric acid is used in the form of cream of tartar is used in bakery industry as a foam stabilizer, Acetic acid in the form of vinegar is used in pickling and curing and Citric acid is used for sugar inversion, prevent
crystallization in confectionery industry and also serves as a preservative.

**Buffers**

Control of pH is a very important step in food industries and in food preparations. In the manufacture of bread, control of pH (between 4.5 and 5.0) is required for the action of amylases on wheat starch. In the processing of fruits and vegetables, if pH is not controlled, browning occurs and there may be change in the colour of green vegetables. Stability of jellies is pH dependent. The activity of enzymes in the manufacture of products like vinegar and cheese is regulated by pH control.

The pH stability is achieved through a buffer system. Buffer solutions have the ability to maintain a relatively constant pH when small amounts of acids or bases are added to them. Strong acids and bases are unsuitable for this purpose. A buffer solution contains a weak acid and a salt of that acid or a weak base and one of its salts. For example, a solution of acetic acid and sodium acetate contains a large excess of both undissociated acetic acid and acetate ions. When a small amount of base is added, the undissociated acetic acid reacts with the hydroxide ions to form water and more

\[
\text{OH}^- + \text{CH}_3\text{COOH} \rightarrow \text{H}_2\text{O}^+ + \text{CH}_3\cdot\text{COO}^-
\]

The addition of a small amount of acid produces a reaction with some of the excess acetate ions.

\[
\text{H}_3\text{O}^+ + \text{CH}_3\cdot\text{COO}^- \rightarrow \text{H}_2\text{O} + \text{CH}_3\cdot\text{COOH}
\]

Both of these reactions go virtually to completion because the reverse reaction has very little tendency to take place, water being
very weak both as an acid and as a base. The result is that the solution can resist pH change by removing both the acids and bases (in reasonable amounts) that are added to the solution.

Lecture 13
Sweeteners
Classification of sweeteners:

Sweeteners

Bulk

Intense (non-nutritive)

Nutritive Sugar replacements, polyols or sugar alcohols
Sugars (Refined sugar, sucrose (Sorbitol, Mannitol, xylitol, Fructose, glucose, dextrose Isomaltate)
Maltose)

Natural /of plant origin Synthetic

(Glycyrrhizin, Steviosides, thaumatin) (Aspartame, Saccharin, Acesulfame K, Sucralose Cyclamate etc.)

Bulk Sweeteners:

* Confer body and texture to foods.
* Completely metabolized by the body and hence contribute energy or calories.
**Intense sweeteners:**

* High intensity sweeteners because a small part is needed to achieve the same sweetness as provided by large amount of sugar.
* They are also referred as non-nutritive sweeteners or sugar replacers or sugar substitutes or alternative sweeteners.
* Used in management of diabetes, dental caries, and weight gain.

**Artificial Sweeteners and their characteristics**

<table>
<thead>
<tr>
<th>Sweetener</th>
<th>Sweetness (sucrose)</th>
<th>Commercial Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acesulfame-K</td>
<td>200</td>
<td>Sweettone, Diabetisweet</td>
</tr>
<tr>
<td>Aspartame</td>
<td>200</td>
<td>Nutrasweet &amp; Equal</td>
</tr>
<tr>
<td></td>
<td>(160-220)</td>
<td></td>
</tr>
<tr>
<td>Cyclamate</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Neotame</td>
<td>10,000</td>
<td>Sweet ‘N’ low Sucaryl etc,</td>
</tr>
<tr>
<td>Saccharin</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Stevioside</td>
<td>300</td>
<td>Sweet leaf Sweet herb Splenda &amp; zero</td>
</tr>
<tr>
<td>Sucralose</td>
<td>600</td>
<td></td>
</tr>
</tbody>
</table>
Maximum permissible limits of various sweeteners in certain food products.

<table>
<thead>
<tr>
<th>Dairy products</th>
<th>Maxlimit of artificial Sweetener (ppm)</th>
<th>Reg. body</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASP</td>
<td>Ace.K</td>
</tr>
<tr>
<td>Sweets - Halwa, Gulab jamun etc</td>
<td>200</td>
<td>500</td>
</tr>
<tr>
<td>Dairy based drinks</td>
<td>600</td>
<td>500</td>
</tr>
<tr>
<td>(chocolate flavoured drink)</td>
<td>3000</td>
<td>1000</td>
</tr>
<tr>
<td>Dairy based desserts</td>
<td>Eg: Ice cream, pudding</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ASP – Aspartic acid
Ack – Acesulphame potassium
Sucra- sucrolose
Sac- sacchain

Table 2:

- Carbonated beverages                     saccharin sodium  100ppm
- Supari                                     Saccharin sodium  4000ppm
- Pan masala                                  Saccharin sodium  8000 ppm
- Pan flavouring material                    Saccharin Sodium  8%
- Carbonated water                           Aspartame        700ppm
- Carbonated water                           Acesulfame potassium300ppm
Regulation:

* PFA rule 47: Strictly condemns utilization of artificial sweeteners in any food except in foods like carbonated beverages, pan masala.
* PFA rule 42: It specifies that every product which is allowed to contain artificial sweetener must have a clean label showing (For table top sweeteners).

“contain--------/name of artificial sweetener)” Not recommended for children.

For Eg: Aspartame releases phenyl alanine so it should be clearly mentioned that “Not for phenyl ketonurics “.

Some of the sweeteners:

1. **Saccharin**: Unsurprisingly N-methyl saccharin is not sweet. The replacement of “co” by so₂ group retains sweetness.

   ![Saccharin structure](Attached)

2. **Acesulfame –K**:
   Reaction of butyne and fluorosulfonyl isocyanate led to the synthesis of dimethyl compound but subsequent synthesis of further dihydro oxathiazinone dioxides which led to other compounds including Acesulfame-K

   ![Acesulfame-K structure](Attached)
3. **Nitro anilines:**

![Nitro aniline structure]

Eg: P-4000(R=O(CH₂)₂CH₃) sweetest compound known to man but commercially useless due to carcinogenic nature.

4. **Aspartame:**

(L-asparyl –L-phenyl alanine methyl ester)

\[
\text{H}_2\text{NCH} – \text{CONH} – \text{CH} – \text{COOCH}_3
\]

5. **Designer sweeteners:**

Eg: Superaspartame (8000 times sweet as sucrose ) formed from aspartame and cyanosuosan other sucronomic acid (2 lakh times more sweeter than sucrose)

6. **Naturally occurring sweeteners:**

a. Monellin – 2aminoacid units – 300 times more sweet
b. Thaumatin-750 times more sweet
c. Miraculin - a glycoprotein
d. Circulin –fruits of Curculigo latifolia, a polypeptide
e. Stevioside – leaves of Stevia rebaudiana – 300times
f. Glycyrrhizic acid – leguminous plant –50 times Glycyrrhiza glabra
7. **Urea based sweeteners:**
   Eg: Dulcin (250 times sweeter than sucrose)

8. **Oximes:-**
   - 450 times sweeter than sucrose
   - Perillartine (Perillaldehyde oxime) is the purified oil from a plant Perilla namkinesis.

9. **Isocoumarins:**
   * Phyllodulcin isolated from the leaves of Hydrangea macrophylla and 200-300 times as sweet as sucrose.
   * It is a 3,4 – dihydro isocoumarin derivative.

10. **Dihydro chalcones (DHC):**
    The parent compound is dihydrochalcone (sweet) prepared from citrus fruits.
    * Naringin DHC
    * Neohesperidin DHC
    * Hesperidin DHC

11. **Sulfamates:**
    These are prepared or manufactured from N-cyclohexyl sulfamate.

**Toxic effects:**
1. **Saccharin:** Even though this is the first synthetic sweetener it leaves a bitter and unpleasant after taste.
2. **Cyclamates:** Sodium & calcium salts of cyclamic acid does not leave any after taste. But the use of cyclamates has been banned as it results in the formation of cyclohexylamine a potent bladder carcinogen is rats.
3. **Acesulfame K**: Used in baked foods, gums, gelatin desserts & soft drinks. In 1998 FDA allowed this chemical thereby increasing consumer exposure. Acesulfame K is not digested hence no calories. It is also found to be a carcinogen.

4. **Aspartame**: It is used in diet foods & low calorie frozen desserts produced from aspartic acid & phenylalanine.

5. **Sucralose**: Derived from sucrose (1998). It is not absorbed through the gut. In 1999 FDA approved it for general usage.

6. **Neotame**: (FDA approved)
   - It is also safe for phenyl ketonurics.
   - It is metabolized & completely metabolized & hence does not accumulate in the body.

7. **Alitame**: A dipeptide of aspartic acid without phenylalanine. It is being used in China, Mexico and New Zealand.

8. **Dulan**: Slightly carcinogenic


10. **Tropical African fruits**:
    a. Kutemfe –2proteins → Thaumatin I ,II
    b. Serendipity berry → Monellin (protein)
    Unstable to heat & loose sweetness at P^H^-2.

**Lecture 14**

**Anti caking Agents**

Some food products such as common salt, dehydrated vegetable powders and fruit powders, soup & sauce powders and baking powder etc tend to cake into hard lumps during damp weather. Anticaking agents help to prevent particles from adhering to each other and turning into cold chunk during damp weather.

These materials function by readily absorbing excess moisture by coating particles to impart a degree of water repellency or making particles insoluble.
Eg: Calcium silicate

It can absorb liquids in amounts two and half times its weight and still remain free flowing. In addition to absorbing water, some anti caking agents effectively absorb oils & other non-polar organic compounds.

Calcium silicate is used to prevent caking in baking powder, table salt & other food ingredients. It is also useful as anti caking agent in complex spice mixtures containing essential oil.

Other anti caking agents are:
Sodium silico aluminate
Tricalcium phosphate
Magnesium silicate
Magnesium carbonate.

Humectants
These are additives which are hygroscopic in nature and acts as moisture retaining agents.

Functions:

* Control viscosity, texture and bulking.
* Reduction of water activity.
* Control crystallization
* Improvement or retention of softness.
* Improve the rehydration of dehydrated form & solubilization of flavor compounds.
Eg: Polyhydric alcohols -- water soluble & hygroscopic

- Propylene glycol (CH₃.CH₂.OH.CH₂.OH)
- Glycerol
- Sorbitol
- Mannitol (CH₂.OH(CH₂.OH)₄.CH₂.OH)

Lecture 15
Flavour and Flavour enhancers
Flavours are of two kinds- natural and artificial.
*Natural flavours* include Spices, herbs, fruit juices and certain plant extracts like menthol from mint and citral from lemon grass. The most natural form of flavor additives available in the food industry are Whole fruit, crushed fruit, purees and concentrates.

*Synthetic flavours*: They include aliphatic, aromatic and terpene compounds. Artificial flavourings are again subdivided into nature identical and synthetic molecules
Eg: 4-hydroxy-3-methoxy Benzaldehyde, 1-menthol

*Another group of natural flavourings obtained by extraction from certain plant products –* vanilla beans, Licorice root, lemon peel, coffee, cherry etc., which are generally extracted in the form of alcoholic infusion

**Typical synthetics**
They are synthetics like
Iso amyl acetate - banana- Beverages
Cinnamaldehyde- cinnamon-candies
Citral-lemon- beverages
Menthol-mint-Gums and candies
Allyl caproate-pineapple-Gums and candies
Diacetyl-Butter-Margarine
Methyl anthranilate-Grapes-soft drinks, candies, jams
Different classes of flavours

Essential oils
They are volatile. They are concentrated hydrophobic liquids containing volatile aromatic compounds extracted from plants. Hydro distillations are used to extract the materials.

Absolutes
They are non-volatile. They are concentrated aromatic oily mixture extracted from plants through solvent extractors. They are obtained from wax like masses called concretes (high mol wt) from plant tissue. Absolutes are low molecular weight compounds.

Fruit Flavours with other natural flavours (WONF)
Fruit concentrates or extracts fortified with naturally occurring plants for wines and cordials

True fruit flavours
They are composed of fruit juices and their concentrates

Artificial fruit flavours
Fruit concentrates fortified with synthetic materials

The following agents are prohibited under the rule number 63A of PFA

- Coumarine
- Tonka bean
- Beta asarone
- Cinnamyl anthranilate
- Estragole
- Ethyl methyl ketone
- Ethyl-3-phenyl glycidate
- Eugenyl methyl ether
- Methyl Beta naphthyl ketone
- P-propyl anisole
- Saffrole and Iso saffrole
- Thujone
**Flavour Enhancer:**
A flavor enhancer is a substance that is added to a food to supplement to enhance its taste or aroma. The most commonly used enhancer is MSG (Disodium and mono sodium glutamates), Yeast extract ,IMP and GMP.

- MSG was discovered in 1908 by Prof. Kikunao Ikeda in soups in Japan. Nearly 400000 tonnes of MSG is manufactured in about 15 countries.
- These flavor enhancers contribute a specific taste/flavor called Umami.
- Glutamate is present in foods like Milk, Cheese, Meat in the form of bound glutamate while in tomatoes, mushrooms and peas it is in the form of free glutamate.
- Nucleotides are predominantly found in meat, poultry and sea foods.

**Toxic effects**
- MSG should not be added to foods intended for children <12months
- MSG is a Excitotoxin-a toxin composed of excitatory amino acids that can cause sensitive neurons to die
- Large doses of MSG can lead to cardiac attack
- Sudden short term reactions like asthma, Headache, Burning, Facial tightness, nausea and Tingling altogether are referred as MSG symptom complex or Chinese restaurant syndrome.

**Lecture 16:**
**Clarifying Agents**

The agents which bring about clarification are called clarifying agents. The clarifying agents are used to remove some solid substances which give hazy appearance to liquids.
Eg: Beer, Carbonated drinks
The sparkling clarity of these beverages is due to clarifying agents. Pectin is a complex carbohydrate present in fruits. It forms a three dimensional fibrillar network. To remove pectin, fibrous tissue and some hemicelluloses where cereal malt is used as a base clarifying agents are used to achieve clarity as they would give turbid appearance to the beverages.

**Natural clarifying agents:**

1. **Activated carbon:** By adsorption some of the suspended particles can be removed.
2. **Gelatin**
   * Prepared from collagen of animals
   * A positively charged protein
   * But it discolours the food hence tannins are used along with it.
   Eg: for Apple & cashew apple juices

Colloids present in the juice coagulate and form a flocculant precipitate which settles down. It is due to electrostatic attraction between positively charged gelatin & negatively charged (pectin) colloids. Hydrogen bonds are formed between phenolic group of juice & peptide group of gelatin.

3. **Albumin:**
   * From egg white
   * Albumin (2%) + juice heated to 91°C
4. **Casein:**
   2% casein solution is added which is precipitated due to acids in juice (24hrs).
5. **Mixture of Tannin + Gelatin:**
   Tannin is used to minimize the bleaching action of gelatin

\[ \rightarrow 42 \text{g tannin} + 85 \text{g gelatin} + 455 \text{Lt} \]
\[ \rightarrow \text{After 18-24 hrs leads to coagulation} \]
* Clear juice is then siphoned off
* Some enzymes are used to bring about clarification
  - Pectinol
  - Filfragol

Pectin digestive enzymes present in the form of pectin methyl esterase are used digest pectins. Apart from this physical methods like freezing and heating can also be used.

**Curing Agents**

These are additives to give the desirable colour, flavor, and discourage growth of micro-organism & prevent toxin formation.

Functions:

1. Colour stabilization – Preserves red colour of meat.
2. Impart softness or tenderness
3. Antibotulinic activity – inhibits the growth of clostridium botulinum.
4. Characteristic flavor.
**Harmful effects:**

N-Nitrosamines are formed in roasted & smoked meats which are potent carcinogens. Nitrosamines are formed by the reaction of secondary and tertiary amines.

\[
\begin{align*}
\text{CH}_3 & \quad \text{NH} + \text{NO}_2 \rightarrow \text{N} - \text{N} = \text{o} \\
\text{CH}_3 & \quad \text{Dimethyl amine} \quad \text{N-Nitroso dimethyl amine}
\end{align*}
\]
Other curing agents:

*Sodium tri poly phosphate
*Sodium hexa metaphosphate

**Cure accelerators** increase the rate of release of nitric oxide formed and helps in the formation Nomb.

   Eg: sodium erythorbate
   Sodium ascorbate