CLARIFICANT USED IN SUGAR PROCESSING

Subhash Chandra

Lime

- Lime is clarifying agents are used in the chemical treatment of sugar cane juice for the manufacturing of plantation white consumption sugar.

- Lime used for clarification should be fresh, good purity and reactivity and free from grits and stones.
- Wherever process of juice clarification is followed, lime is the main clarification agent. Lime is usually added to the juice as Milk of lime, a white milky liquid containing slaked lime in suspension and in solution.
- In some part of world, however the clarification agent is partly hydrated lime which is added to the juice a fine dry powder.

SPECIFICATION

Sr.	PARAMETER	LIMIT(%)
1.	CaO content	>90
2.	Acid insoluble silica	<1.5
3.	Iron as Fe_2O_3	<2.5
4.	Magnesium, as MgO	<2.0
5.	Aluminium as Al_2O_3	<1.0
6.	Dead Burnt Lime	<1.0
7.	Sulphates$(SO_4)^{--}$	Absent

- Lime first neutralizes the free organic acids present in cane juice, forming calcium organic salt.
- Lime reacts with phosphoric acid present in cane juice and forms tri-calcium phosphate of formula $Ca_3(PO_4)_2$
- Lime combines with nitrogenous impurities and partly precipitated.
- Lime reacts with cane juice and removes coloring matters like chlorophyll and anthocyanin.
- Lime reacts with cane juice and SO_2 to form precipitate of calcium sulphite $CaSO_3$.
- When lime is added some of it undergoes reaction and some remains in solution in the form of soluble CaO.

- Lime is the oldest and cheapest chemical being used in sugar manufacture, as a juice Clarificant. The quantities consumed depend on the process adopted for clarification such as—
- *(i)* for defecation consumption is 0.08 to 0.1% cane.
- *(ii)* for sulphitation 0.12 to 0.15% cane.
- *(in)* for carbonation 1.5 to 2% cane.
- In Indian factories lime ie. calcium oxide CaO is used in the form of lumps or powder but in Louisiana hydrated lime i.e $Ca(OH)_2$ in powder form or pulverised quick lime has replaced the lumps completely. Lime is obtained from high grade limestone by burning it in kilns. Many Indian sulphitation plants prefer producing lime in kilns, installed at the factory site procuring limestone and coal, for their process use.

Lime stone i.e. calcium carbonate when heated is decomposed with the formation of calcium oxide and carbon dioxide.

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$100 \qquad 56 + 44$$

Thus pure calcium carbonate on dissociation will yield 56%, CaO. The reaction is endothermic heat absorbed being 42.5 K Cal. per mole. The optimum temperature range is 1100°C to 1300°C, though the dissociation commences at 600°C. Burning at temperatures exceeding 1350°C for longer periods results in production of dead burnt lime'. Higher SiO_2 or MgO content in limestone can cause formation of 'dead-burnt' lime even at 1200°C. Properly burnt lime is highly porous, light in weight and slakes quickly to form Calcium hydroxide i.e. $Ca(OH)_2$ on account of the easy penetration of water molecules in the atomic interspaces

Lime i.e. CaO is highly hygroscopic and forms calcium hydroxide on reacting with water.

$$CaO + H_2O \rightarrow Ca(OH)_2 + 15.2\ KCal$$

The reaction is exothermic and heat is evolved during reaction.

SULPHUR

Sulphur is an important chemical used in plantation white sugar manufacture for generating SO_2in the clarification house. Elemental sulphur occurs mostly in U.S.A., Italy and Japan, though in sulphide form it is found in copper, iron and other mineral deposits. The atomic weight of sulphur is 32.06 while its melting point is 113°-115°C At 444.7°C which is the boiling point of sulphur at ordinary pressure sublimation occurs. For use in sugar manufacture sulphur must be of very high purity (above 99%)., the maximum permissible levels of impurities being—

(i) Moisture-1%,

(ii) ash 0.1%,

(iit) bituminous matter -0.1%,

(iv) arsenic 0-05%.

Sulphur has an atomic weight of 32.06 and melts at 113°C. It vapourises at 444°C when heated out of contact with air. On account of its self sustained burning characteristic a mass of pure sulphur once ignited burns completely in air.

In fact in one simple practical test a small quantity of sulphur to be used in factory is ignited in a silica dish and if the entire mass is burnt out in air the quality of sulphur is considered satisfactory. Presence of impurities is indicated by formation of a dark layer on the surface which hinders combustion by restricting supply of oxygen (i.e. air).

Sulphur dioxide — Combustion of sulphur in a current of air generates sulphur dioxide SO_2.

When sulphur is heated in air it first melts and at about 363°C burns with blue flame producing So2 and traces of SO_3.

$$S + O_2 \longrightarrow SO_2 + 2217 \text{ kcal/kg}$$

Sulphur dioxide is a colourless gas 2.264 times heavier than air and possess an obnoxious

smell. It is a poisonous gas. It can be liquified under pressure the liquid boiling at -10°C. Molecular weight of SO_2 is 64.06. In the presence of moisture SO_2 is oxidised to SO_3 during the process of combustion of sulphur.

Sulphur dioxide is highly soluble in water, 45 volumes being soluble in one volume of water. However, a saturated solution of sulphur dioxide in water when boiled expels So2 completely.

It combines with water to form sulphurous acid.

$$H_2O + SO_2 \longrightarrow H_2SO_3$$

If the SO_2 contains traces of So3 some sulphuric acid is formed

$$H_2O + SO_3 \longrightarrow H_2SO_4$$

The sulphurous acid is dibasic and forms both normal and acid salts.

$$H_2SO_3 \longrightarrow H^+ + HSO^{-3} \quad \text{Hydrosulphiteion}$$

$$H_2SO_3 \longrightarrow 2H^+ + SO^{3-} \quad \text{Sulphite ion}$$

Sulphur dioxide bleaches juice by acting on the coloring matter. Sulphurous acid is a strong bleaching agent. It bleaches the coloring matter originally present in the cane juice. It prevents or slows down the color formation in later stages of the processing. It reduces the ferric salts which are highly colored compounds formed by the action of iron of the equipment with polyphenols into colorless ferrous compounds. Sulphur dioxide gas decreases the viscosity of the juices. The lower the viscosity of juice, the easier is crystallization.

Advantage of sulphitation - The advantages of sulphitation are presented as follows (Hugot, 1986):

- The mud settles more rapidly and hence improved capacity of clarifiers
- The mixture of sugar crystals and molasses before centrifuging (massecuites) are less viscous and boil faster.
- Better crystallization in consequence.
- There is a marked improvement in the color of the sugar, there appears to be a significantly reduced transfer of color from the mother liquor into the crystal.
- There is a slight gain in the capacity of centrifugals.
- Better elimination of phosphates and waxes leading to better refining quality and filterability of the sugar produced

Action of SO_2 on juice clarification

SO_2 neutralizes the excess quantity of lime added and precipitates calcium sulphite.

$$Ca(OH)_2 + H_2SO_3 \longrightarrow CaSO_3 + H_2O$$

If more SO_2 gas is passed and the juice is made slightly acidic, part of calcium sulphite is converted into soluble calcium bisulphite, which is undesired.

$$CaSO_3 + H_2SO_3 \longrightarrow Ca(HSO_3)_2$$

Further addition of lime increases the pH and precipitation of calcium sulphate starts again. The precipitation is complete when all the acidity is neutralized by lime.

$$2H_2SO_3 + 2Ca(OH)_2 \longrightarrow CaSO_3 + 4H_2O$$

If highly acidic juice containing the soluble calcium bisulphate in solution is boiled, it again decomposes into precipitated calcium sulphate and sulphure dioxide.

$$2Ca(HSO_3)_2 \longrightarrow CaSO_3 + SO_2$$

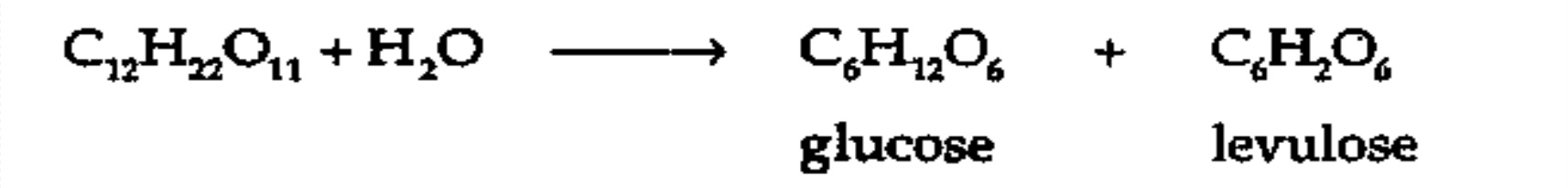
Disadvantages of Sulphitation

Kulkarni (2010) reported the demerits of sulphitation process that the use of the sulfur burner is difficult as it causes the toxic SO_2 to be released into the atmosphere, leading to serious environmental pollution.

It can also create health problems for the workers handling the sulfur burners. The low color sugar and good luster obtained from syrup sulphitation is a temporary one. The color can increase from 60 IU to 100 IU or even 120 IU within 6 to 10 months (Kulkarni, 2010).

Reducing Sugars

Sucrose is fairly stable at high pH, but undergoes decomposition when subjected to low pH. Sucrose is hydrolysed at low pH into reducing sugars following the reaction.



This reaction is catalysed by hydrogen ions and the rate of hydrolysis is higher, higher the temperature and lower the pH. Thus pH below 7.0 is to be avoided in all the treatments of juice in clarification to prevent inversion since the above reaction is irreversible.

The juices normally contain 0.5 to 1% reducing sugars which play vital role in determining the exhaustion potential of molasses in the final phase of crystallisation. Reducing sugars also have to be kept intact to obtain maximum crystallisation of sucrose in final boiling. Reducing sugars are more reactive than the sucrose/ and unlike the latter are unstable at high pH. High temperature accelerates this decomposition. Out of these two hexoses,fructose is more sensitive to alkaline conditions and is decomposed more rapidly than glucose. When reducing sugars are reacted upon by alkali, fructose is destroyed first while more fructose is formed from glucose in accordance with Lobry De Bruyn Van Ekenstein transformation, whereby equilibrium of glucose and fructose is maintained in alkaline medium.

The decomposition of reducing sugars in alkaline condition results in formation of lactic, gluconic, saccharanic and oxalic and other organic acids which combine with lime to form calcium salts. While salts like calcium oxalate and calcium lactate are stable some other organic acid salts decompose into acids under influence of heat. Under mild alkaline condition slightly coloured acids like lactic acid are formed. At higher

At higher temperatures, the acids formed, combine with lime to form coloured compounds. Thus the decomposition of reducing sugars has to be avoided for following reasons—

(i) Organic acids are formed which increase calcium content of juices,

(ii) The salts of organic acids increase scaling of evaporator,

(iii) Dark coloured compounds are formed which increase colour content of juice,

(iv) Exhaustibility of molasses is adversely affected.

The conditions under which sucrose remains stable are contrary to those for reducing sugars and therefore as far as possible pH close to 7.0 should be maintained and the time of contact at high or low pH should be minimal. Particularly at high temperatures minimum time of reaction is essential when pH deviates from 7.0 either way

Phosphate—As stated earlier phosphate precipitation after reaction with lime is the main reaction responsible for juice clarification. The reactions between lime and phosphates take time for reaching equilibrium and are rendered more complex in nature in juice due to th npounds. Lime rea

(*i*) $Ca^{+2} + HPO_4^{-2} \rightarrow CaHPO_4$

(*ii*) $3Ca^{+2} + 2PO_4^{-3} \rightarrow Ca_3(PO4)_2$

Main reaction of clarification –

$$3Ca(OH)_2 + 2H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6H_2O$$

The tricalcium phosphate is transformed into insoluble hydroxyapatite with drop in pH of juice. Formation of hydroxyapatite is accelerated by high temperature and optimum conditions for formation of phosphate precipitate are a. pH of 7.5-8 and b. heating to 100°C.

- 100°C.Cane juice contains phosphates both in ionic and nonionic form in varying amounts from 50-200 mgms per litre and the optimum level of P_2O_5 of 300 ppm.

- The purifying effect is to be caused by the absorptive power of calcium phosphate and it has been observed that calcium phosphate clarification is most effective in eliminating colloids and finely dispersed matter

Phosphoric Acid

Phosphoric acid and phosphates are used in the sugar industry for various purposes, which mainly can be classified under two headings:

- The clarification of sucrose solutions
- The conditioning of (feed) water

- The purifying effect is to be caused by the absorptive power of calcium phosphate and it has been observed that calcium phosphate clarification is most effective in eliminating colloids and finely dispersed matter.
- Since the filtering properties of a calcium phosphate precipitate are, however, unsatisfactory, low pressure (bag) filters or flotation process is preferred to filter presses

SPECIFICATION

Sr. No.	PARAMETER	LIMIT
1.	PHYSICAL APPEARANCE	COLORLESS VISCOUS LIQUID
2.	PURITY AS H_3PO_4	85.0
3.	P_2O_5 CONTENT,MIN	61.5
4.	IRON(PPM) MAX.	3000
5.	SULPHATE AS(SO_4)%	1.25
6.	SPECIFIC GRAVITY AT25°C	1.7

The advantages from adding phosphate are:

- Clearer juice
- Greater colloid elimination
- Fewer lime salts in clarified juice
- More rapid settling
- Faster mud filtration
- Better colour of sugar

SUGGESTION

Always use food grade phosphoric acid for process industry. Fertilizer grade phosphoric acid contains sulphate. Hence if phosphoric acid gives white, thick precipitate with barium chloride solution it should be rejected. If turbidity is observed the sample should be analyzed for its phosphate and sulphate content before use in the process.

Color Precipitant

This is relatively new process aid, color precipitant are does not reduce the conc. of color forming constituents such as amino acid & polyphenols . As the ppt. formed by color coagulant has to be removed, it should be added either before lime addition or flocculent addition .

Color coagulant is characterizing by a strong basic centre coupled with a long chain hydrocarbon or some times a polymer chain.

Optimum dose has to be determined in the lab by determining color of sugar solutions.

For Untreated syrup - Dose 100-150 ppm

For Untreated Melt - Dose 250-300 ppm

Mill Sanitation Chemical

Target of MSC is to increase sucrose recovery, reducing dextran formation, fructose degradation products, organic acids as well as bad odour during the manufacture of sugar, by control over various micro-organism like leuconostoc mesenteroids and leuconostoc dextranicam.

Generally MSC used in three forms-

1. Di-thiocarbamate (Na/K dimethyl di thio carbamate)
2. Quaternary ammonium compound (Benzalkonium chloride)
3. Halogen based (Sodium hypo chlorite, chlorine di oxide)

Specification

Sr.No	Chemical	Requirement
1.	Di-thio carbamate	i. Yellow appearance ii. pH value 9-10, iii. Active content 35-40
2.	Quaternary Ammonium Compound	i. Colorless liquid ii. pH 8-9 iii. Active content 30-35
3.	Halogen based	i. Colorless liquid ii. pH value 10-11 iii. Cl content 15-20

Optimum Dose

Optimum dose of Mill Sanitation Chemical is depend upon the RS and dextran content in primary juice. Tentative optimum doses of MSC per ton of crush cane is follows-

Sr.No.	CHEMICAL NAME	ACTIVE CONTENT(%)	DOSE ppm ON CANE
1.	Di-thio carbamate	35-40	12-15
2.	QAC	50	4-5
3.	Halogen Based	25	10-15

Benefit

1 . Increase in sugar recovery by reducing loss of sucrose to 0.10-0.20 kg/ton of cane as against loss of sucrose 0.2-1 kg/ton of cane if MSC are not used.

2. Reduction in formation of dextran on mills leading to less dextran content in intermediated sugar product.

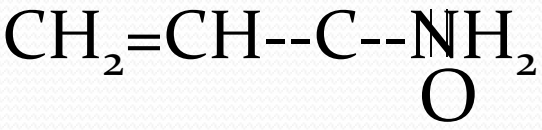
3. Reduction in color forming precursors such as fructose degradation product.

FLOCCULANT

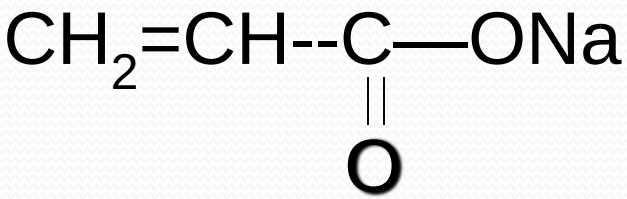
These are special synthetic flocculating agents. Now generally called polymer flocculants .

- The polyelectrolyte are mostly ployacrylamides,anionic and of high molecular weight.
- Action of these polyelectrolyte is to produce the secondary flocculation.

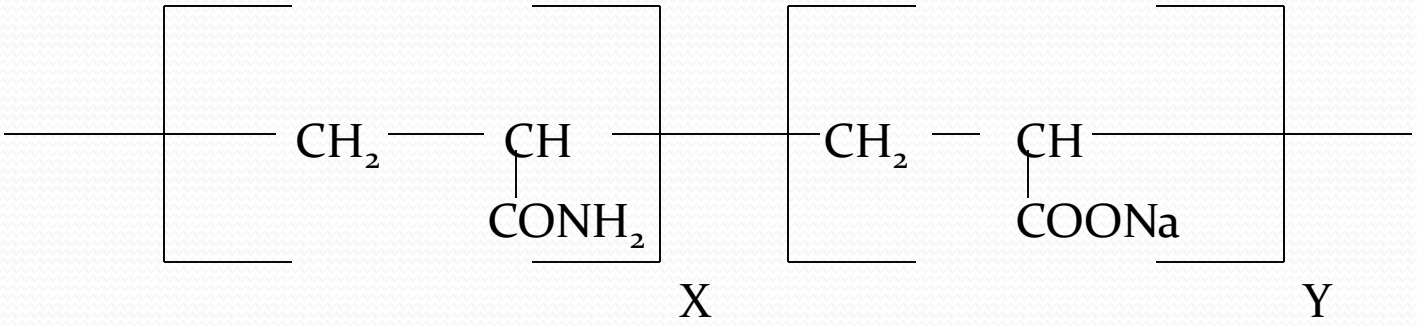
FORMULA



Acryl amide



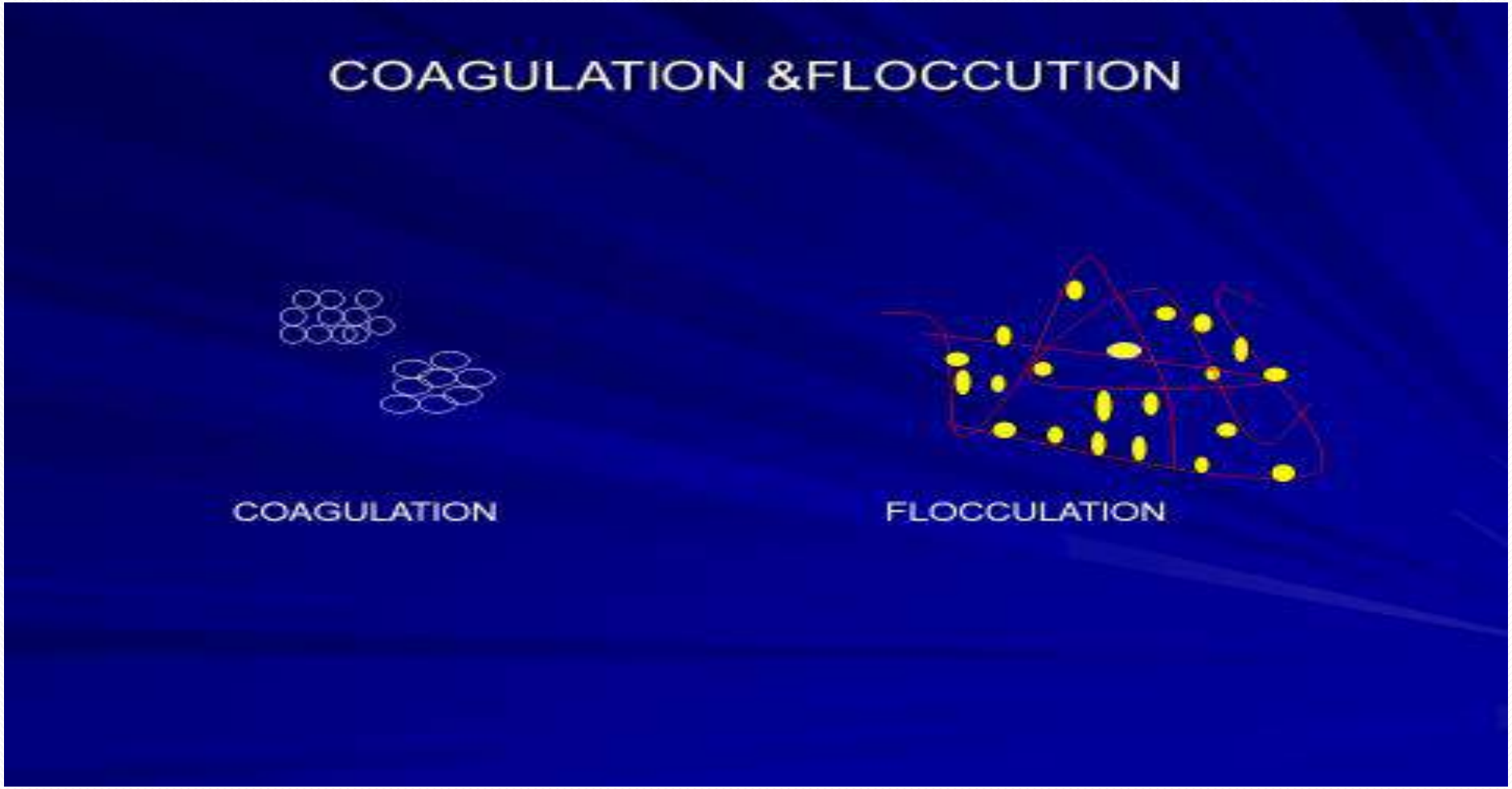
Sodium acryl ate



POLYACRYLAMIDE CHAIN

Bridging Theory Of Flocculation -

Flocculant act as a chain, the chain molecules form interparticle bridges and bind the particles together.



Effect Of Molecular Weight-

- *All polymer flocculants are of high m*olecular weight.
- Rate of settling is a function of molecular weight, i.e. settling rate increased with increasing molecular weight.
- Molecular weights below 106 act only as stabilizers and are not large enough for bridging.
- Molecular weights should be on the order of 107 for good clarification.

Benefits-

- A good flocculent benefits are:
- It improves flocculation
- Increases settling rate
- Reduces mud volume
- Decrease Pol in cake
- Most important, increases the clarity of the clarified juice and melt.

Viscosity Reducers-

Target of viscosity reducers is to increase fluidity of mother liquor by lowering viscosity of massecuite, reducing surface tension leading to improvement in boiling house efficiency,crystallisation, centrifugation & exhaustion of molasses.

Benefits-

- Reduce time for C-Boiling.
- Better purging, less washing.
- Reduce ash content on sugar.
- Better molasses exhaustibility in quality & quantity.
- Higher sucrose recovery.

Chemical Nature -

These are surface active chemicals. These compound are generally organic compounds with high molecular weight.

Optimum Dose -

Optimum Dose has to be determined by carrying out efficiency test in the laboratory.