# EFFECT OF CHEMICAL TREATMENT ON PLASTICITY RETENTION INDEX OF BLOCK NATURAL RUBBER

A DISSERTATION SUBMITTED TO THE UNIVERSITY OF KERALA
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

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## CHEMISTRY

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***BY***

***JYOTHI NATARAJ***

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**POST GRADUATE DEPARTMENT OF CHEMISTRY**

**SANATANA DHARMA COLLEGE**

**(Accredited at FOUR STAR level by NAAC)**

**Alappuzha 688 003**

**June 2007**

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# CERTIFICATE

This is to certify that the work described in this dissertation titled "Effect of chemical treatment on plasticity retention index of block natural rubber" is an authentic record of the work done by JYOTHI NATARAJ Register No 05 125 003 doing MSc programme in Chemistry in S.D.College, Alappuzha under my guidance and supervision.

Head of the Department

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## CERTIFICATE

This is to certify that the report ***Effect of Oxalic acid treatment on Plasticity Retention Index of Raw Natural Rubber*** is a bonafide record of the work undertaken by **Kum. Jyothi Nataraj**, M.Sc. Chemistry, S.D.College, Alappuzha under my supervision and guidance, in partial fulfillment of the requirement for award of Masters degree in Chemistry. Also certified that the results obtained in this study have not been used for the award of any other degree or diploma.

Dr.M. Sunny Sebastian,
Joint Director (P &QC)

# DECLARATION

I hereby declare that the project report entitled "EFFECT OF CHEMICAL TREATMENT ON PLASTICITY RETENTION INDEX OF BLOCK NATURAL RUBBER" is an authentic record of the original work done by me under the supervision of Mr. M. Sunny Sebastian, Joint Director, Central Laboratory RRII, Kottayam and Dr. C.Krishnakumar, Department of Chemistry, S.D.College, Alappuzha.

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I wish to express my sincere thanks to all the staff of Central Laboratory RRII, Kottayam and acknowledge the cooperation and help extended by all teaching and non teaching staff of Chemistry Department, S.D.College, Alappuzha. The help by all my friends in the college are sincerely appreciated.

JYOTHI NATARAJ

# SYNOPSIS

Natural Rubber is a high molecular weight polymer with viscoelastic properties. Structurally it is cis – 1, 4 poly isoprene which has density of 0.93 gm $cm^3$ at $20^0$ c. The main use of Natural rubber is in automobiles. First chapter gives the Introduction of Natural Rubber, various marketable forms of Natural Rubber, Review of literature and processing of Technically specified Rubber.Second chapter deal with the experimental methods to find out the Initial wallace plasticity ($P_o$) and plasticity Retention Index (PRI). Po is a measure of the plasticity of the rubber which indirectly gives the estimation of the polymer molecular chain (or molecular weight). PRI was developed as a simple rapid method of measuring the resistance of raw rubber to oxidation.

Third chapter describes the effect of various chemicals. On PRI of raw natural rubber. $P_o$ and PRI of the sample were found out by soaking fresh sample in 0.1%, 0.2% and 0.4% oxalic acid for 30 minutes. Again $P_o$ and PRI of the sample were found out using 0.1 % oxalic acid by changing the duration of soaking. That is, 10 min, 20 min, 30 mints. At last $P_o$ and PRI of the sample were found out using sodium oxalate and potassium oxalate. Results and discussion and conclusion are included in the 4th and 5th chapter. From the experiments done it was found that soaking of wet crumb in oxalic acid, sodium oxalate or potassium oxalate can improve the PRI of raw natural rubber. The optimum concentration and duration of soaking was found to be 0.1% and 10 minutes respectively. The Reactivity of oxalate is in the order.

Potassium Oxalate > sodium oxalate > Oxalic acid

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# CHAPTER - I

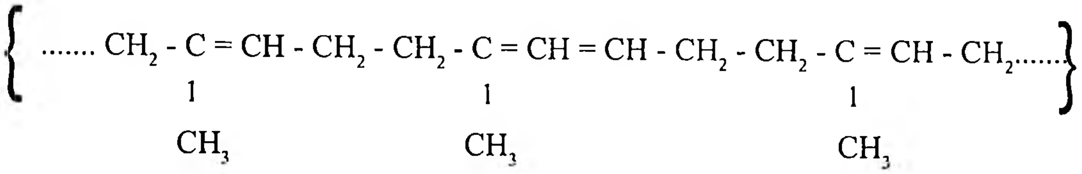
# INTRODUCTION

## 1.1 NATURAL RUBBER

Hevea Brasiliensis is the most important commercial source of natural rubber-a product of vital importance recovered from its latex.

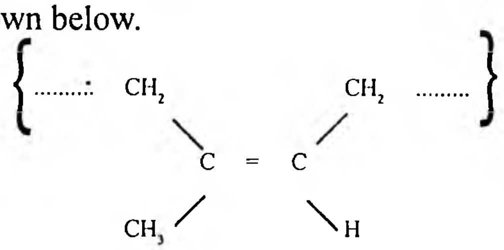
Natural rubber however has been found in the latex of over 2000 species of plants belonging to 311 genera of 79 families. The minor sources of natural rubber are Manhot glazione (Euphorbiacea), ficus elastica (Moraceac), parthenium argintatum and Taraxacum Koksaghyz (compositac). In addition, many other species like Euphorbia intisy (Enphorbiaceae), Cryptostegia grandiflora madagascariensis (Asclepiadacea), Funtumia elastic, etc have been experimented as possible minor sources of natural rubber.

Natural Rubber (NR) is a high molecular weight polymer with viscoelastic properties. Structurally it is cis -1,4 poly isoprene which has density of 0.93 gm $cm^3$ at $20^0c$. The structural formula of polyisoprene $(C_5H_8)_n$ is shown below.

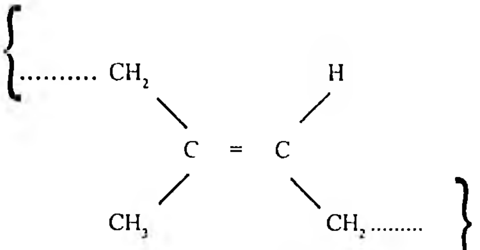


$$\left\{ \cdots\cdots CH_2-\underset{\substack{|\\ CH_3}}{C}=CH-CH_2-CH_2-\underset{\substack{|\\ CH_3}}{C}=CH=CH-CH_2-CH_2-\underset{\substack{|\\ CH_3}}{C}=CH-CH_2\cdots\cdots \right\}$$

Because of the presence of olefinic carbon atom, cis and trans forms are possible. The trans form of polyisoprene is called "guttapercha". Both cis and trans forms are shown below.



cis - 1,4 - Poly Isoprene
(Natural Rubber)



Trans - 1,4 - Poly Isoprene
(Guttapercha)

Isoprene is a diene and 1,4 addition leaves a double bond in each of the isoprene units. So NR shows all the reactions of an unsaturated polymer. It gives addition compounds with halogens, ozone, hydrogen chloride and several other reactants that react with olefins. Its combination with sulphur is known as vulcanisation. This reaction converts the plastic properties of raw rubber into elastic properties. Vulcanised rubber has very high tensile strength and comparatively low elongation. Its hardness and abrasion resistance are also high compared to raw rubber. Because of these NR finds application in the manufacture of a variety of products.

The main use of Natural rubber is in automobiles. In developed countries nearly 60% of all rubber consumed is for the automobile tyres and tubes. In heavy duty tyres, the major portion of the rubber used is NR. In addition to tyres a modern automobile has more than 300 components made out of rubber. Many of these are processed from NR. Use of NR in hoses, foot wear, battery boxes, foam mattresses, balloons, toys etc are well-known. In addition to this NR now finds extensive use in soil stabilization, in vibration absorption and in road making. A variety of NR based engineering products are developed for use in these areas. [1]

**Table - I**

**Physical properties of Natural Rubber [2]**

| Parameters | Values |
|---|---|
| Specific gravity | 0.92 |
| Refractive Index | 1.52 |
| Coefficient of cubical expansion | 0.00062 /°C |
| cohesive energy density | 63.7 Cal/cc |
| Heat of combustion | 10547.084 Cal/g |
| Thermal conductivity | 0.00032 cal/sec/cm/°c |
| Di electric constant | 2.37 |
| Power factor (at 1000 cycles) | 0.15-0.2 |
| Volume resistivity | $10^{15}$ ohm cm |
| Dielectric strength | 3937 V / mm |

## 1.1a Processing of the Crop

The main crop from the rubber tree is latex, a milky white dispersion of rubber in water, which is harvested by the process of tapping. The latex that flows out is channelled into an attached container. Coconut shells and polythene cups are used as container in most Indian estates. Latex collected in the cup is transferred to clear buckets two or three hours after tapping. Around 80% of the crop from plantation is in the form of latex.

The latex which gets dried upon the tapping panel (tree lace) and the collection cups (shell scrap) also form part of the crop and are collected by the tapper in a basket just before tapping. The latex spilt and/or overflowed on the ground, when gets dried up, is also collected as scrap (earth scrap)once in a month or so. Normally, 15 to 25% of the total crop constitute tree lace, shell scrap and earth scrap, together called field coagulum rubbers.

The different forms of crop are highly susceptible to degradation due to bacterial contamination on keeping. It is essential to process them into forms that allow safe storage and marketing. [3]

## 1.2 Marketable forms of Natural Rubber

The important forms, in which the crop can be processed and marketed are

1 **sheet rubbers**
    i. Ribbed Smoked sheet (RSS)
    ii. Air dried Sheet (ADS)
2. **Crepe Rubbers**
    i. Pale Latex Crepe (PLC)
    ii. Estate Brown Crepe (EBC)
3. **Block Rubber (Technically specified rubber)**
4. **Preserved field Latex**

5. **Latex Concentrates**

   i. Centrifuged Latex
   ii. Creamed Latex

The crop collected in the form of latex can be processed into any of the above forms. But the crop collected as field coagulum can be processed only into Estate Brown Crepe or Block Rubber. [4]

## 1.2a Sheet Rubber

## Processing into Sheet Rubber

Latex is coagulated in suitable containers into thin slabs of coagulum and sheeted through a set of smooth rollers followed by a grooved set, and dried to obtain sheet rubber. Depending upon the drying method, sheet rubber are classified into two: ribbed smoked sheet and air dried sheets (Pale amber unsmoked sheets). A major quantity of rubber in India (about 71%) is marketed in the sheet form at present, as it is the oldest and the simplest method of processing latex into a marketable form.

For processing into sheet rubber, the latex collected is brought to the processing factory before pre-coagulation sets in. In cases where the latex is prone to pre-coagulation an anticoagulant is used. A few drops of the anticoagulant are added to collection cups at the time of tapping, if necessary. The rest of the required quantity is added into the collection buckets when they are half full. Anticoagulants should not be poured into empty collection buckets.

Latex brought to the factory is a strained through 40 and 60 mesh stainless steel sieves. The volume of latex is measured with a standard vessel and calibrated rod. The dry rubber content (drc) is estimated with a metrolac which is a special type of hydrometer calibrated to read drc directly. The drc thus obtained is only approximate and for accurate determination, laboratory methods are employed.

Latex is diluted in bulking tanks of a standard consistently of ½ kg of dry rubber for every litres of diluted latex (12.5% drc) . The diluted latex is allowed to stand in the bulking tank for a fixed time (usually 15 to 20 minutes) to sediment the heavy dirt particles. The diluted latex is drawnout from the bulking tank without disturbing the sedimented impurities into coagulation pans or tanks. Four litres of latex is usually transferred to each pan. [5]

## Coagulation

Formic acid or acetic acid is generally used for coagulation. The quantity of acid required for satisfactory coagulation depends on various factors like the amount and type of anticoagulam used, the duration of coagulation, the season and the nature of the latex. A general indication of acid requirement for coagulation is given in table.

Acid requirement for coagulation of 4 litres of diluted latex containing ½ kg rubber.

**Table - II**

| | Acetic Acid | Formic Acid |
|---|---|---|
| 1. For next day sheeting | 3ml diluted to 300ml with water | 1.5 ml diluted to 300 ml with water |
| 2. For same day sheeting | 4ml diluted to 400ml with water | 2ml diluted to 400ml with water |

However the acid requirement may slightly change under varying conditions and can be fixed up by experience. Only diluted acid should be used for coagulation and it should be thoroughly mixed with latex.

Coagulants like catalyst AC and Sulphuric acid are also being used for planters. Catalyst AC is a dry powder and a comparatively safe coagulant. Normally 100ml of a 5 percent solution of this chemical is enough for making ½ .kg sheets.

Since Sulphuric acid is highly corrosive, care should be taken in its handling and dilution. 300ml of a 0.5% solution of the acid is required for same day sheeting and 250ml for next day sheeting. (A 10% stock solution can be prepared by adding 1 litre of concentrated sulphuric acid to 9 litre of water slowly with stirring 500ml of this solution when added to 9.5 litres of water gives 0.5% solution). Thorough washing of the coagulum during and/or after sheeting is essential to remove acid residues. Retention of sulphuric acid in dried sheets can lead to problems such as tackiness due to oxidation of rubber and retardation of vulcanization of compounds prepared from them. Hence use of sulphuric acid is to be made with utmost care, when other coagulants are not available at an economic price.

Coagulum often shows a tendency for surface darkening. To prevent this, a small quantity of sodium bisulphite (1.2g per kg drc) dissolved in water may be added to the diluted latex before coagulation.

After coagulation the coagulum is removed from the pans or tank and thoroughly washed in running water. They are sheeted either in a sheeting battery or smooth rollers to a thickness of 3mm and finally passed through the grooved roller. While sheeting, the coagula are continuously washed, the sheets are again washed in running water in a tank.

Mould growth on sheets can be prevented by dipping the freshly machined sheet in a dilute solution of paranitrophenol (PNP) for 10-15 minute. The concentration of paranitrophenol is 0.05 to 0.1% in water. 100 liters of the solution will be sufficient for treating 100 sheets.

The wet sheets are allowed to drip on reapers arranged in a well- ventilated dripping shed. Sheets should not be exposed to direct sunlight to avoid development of tackiness. [6]

## Smoking

The sheets after four to six hours of dripping in shade, are put in the smoke house where the temperature is maintained between 40° and 60°c. In the smoke house sheets are dried gradually where by blisters are avoided. In addition, the creosotic substances present in the smoke present mould of yeast growth on sheets.

It is preferable to smoke the sheets on the first day at a low temperature (40° to 30°C). For the subsequent days (i.e. second to fourth day) the sheets are to be dried at a higher temperature (not exceeding 60°C) and fairly low relative humidity. For this the smoke house has two chamber where precise control of temperature and humidity is possible. However, in the absence of two smoke chambers, the sheets can be dried in a single chamber by placing the sheets on the reapers at the bottom region on the first day and at the top regions on subsequent days of smoking.

There are various types of smoke houses, all working on the same general principle. The essential features of a smoke house are a chamber in which the sheets can be placed on reapers, a furnace outside the chamber and a flue duct connecting them. The sheets are to be turned on the reapers every day for uniform smoking and drying and to avoid reaper marks. Four days of smoking is generally sufficient under normal conditions, but during the rainy season five to six days are required for satisfactory drying. [7]

## Grading

The completely dried sheets are removed to the packing shed where they are carefully inspected and graded according to the standards as per IS-15361-2003. This standard provides for six grades of ribbed smoked sheets, viz, RSS IX, RSS 1, RSS 2, RSS 3, RSS 4 & RSS 5

## RSS IX

The grade must be produced under conditions where all processes are carefully and uniformly controlled.

Each bale must be packed free of mould but very slight traces of dry mould on wrappers or bale surface adjust to wrapper found at time of delivery will not be objected to, provided there is no penetration of mould inside the bale.

Oxidized spots or streaks, weak, heated, under-cured, over-smoked and free from blemishes, specks, resinous matter (rust), blisters, sand, dirty packing and any other foreign matter. Small pin head bubbles, if scattered, will not be objected to.

No master or official international sample has been established for this grade.

## RSS 1

Each bale must be packed free of mould but very slight traces of dry mould on wrappers or bale surfaces adjacent to wrapper found at time of delivery will not be objected to provided there is not penetration of mould inside the bale.

Oxidized spots or streaks, weak, heated, under-cured, over-smoked, opaque and burnt sheets are not permissible.

The rubber must be dry, clean, strong, sound and free from blemishes, resinous matter (rust), blisters, sand, dirty packing and any other foreign matter, except slight specks are shown in the sample. Small pinhead bubbles if scattered will not be objected to.

## RSS 2

Slight resinous matter (rust) and slight amounts of dry mould on wrappers, bale surfaces and interior sheets, found at time of delivery will not be objected to. Should "Rust" or "Dry Mould" in an appreciable extent appear on more than 5% of the bales samples, it shall constitute grounds for objection.

Small bubbles and slight specks of barks to the extent as shown in the sample will not be objected to

Oxidized spots or streaks, weak, heated, under-cured, over-smoked, opaque and burnt sheets are not permissible.

The rubber must be dry, clean, strong, sound and free from blemishes, blisters, sand, dirty packing and all other foreign matter other than specified above as permissible.

## RSS 3

Slight resinous matter (rust) and slight amounts of dry mould on wrappers, bale surfaces and interior sheets, found at time of delivery will not be objected to. Should "Rust" or "Dry mould" in an appreciable extent appear on more than 10% of the bales sampled, it shall constitute grounds for objection.

Slight blemishes in colour, small bubbles and small specks of bark permissible to the extent shown in the sample.

Oxidized spots or streaks, weak, heated, under-cured, over-smoked, opaque, and burnt sheets are not permissible.

The rubber must be dry, strong and free of blemishes, blisters, sand, dirty packing and all other foreign matter other than specified above as permissible.

## RSS 4

Slight resinous matter (rust) and slight amount of dry mould on wrapper, bale surfaces, and interior sheets, found at time of delivery will not be objected to. Should "Rust" or "Dry Mould" in an appreciable extent appear on more than 20% of the bales sampled, it shall constitute grounds for objection.

Medium sized bark particles, bubbles, translucent stains, slightly sticky and slightly over-smoked rubber are permissible to the extent as shown in the sample.

Oxidized spots or streaks, weak, heated, under-cured, over-smoked (in excess of the degree shown in the sample), and burnt sheets are not permissible.

The rubber must be dry, firm and free of blemishes, blisters, sand, dirty packing and all other foreign matter other than specified above as permissible.

## RSS 5

Slight resinous matter (rust) and slight amounts of dry mould on wrappers, bale surfaces and interior sheets, found at time of delivery will not be objected to. Should "Rust" or "Dry Mould" in an appreciable extent appear on more than 30% of the bales samples, it shall constitute grounds for objection.

Large bark particles, bubbles and small blisters, stains, over- smoked slightly sticky rubber, and blemishes of the amount and size shown in the sample are permissible slightly under-cured rubber is permissible.

Weak, heated, burnt, oxidized spots or streaks are not permissible.

The rubber must be dry, firm free of blisters, except to the extent shown in the sample. Dirty packing, sand and all other foreign matter other than specified above is not permissible.

The grading of sheets is carried out by visual examination. Normally this is accomplished by holding sheets against light, when the most obvious defects become apparent. [8]

## Air Dried sheets

The sheets dried in hot air are called air- dried sheets. The chamber is heated by blowing air over a set of electric heaters or radiators to which steam is supplied from a boiler. The temperature inside the drying chamber is controlled thermostatically. The number of heaters required depends on the capacity of the drying chamber. During the first two days of drying, the temperature is limited to 37 to $40^0$C, as otherwise the sheets may have a darker shade. During the last two days, the temperature is raised to 62 to $65^0$C. If the design of the chamber is tunnel-type intended for continuous operation, then the temperature at the hot end of the tunnel is maintained at $62.5^0$C and that at the cool end at $37.5^0$C. [9]

### 1.2b Crepe rubber

### Pale Latex Crepe

Pale Latex Crepe (PLC) is produced from latex selected specially under strictly controlled conditions and hence are of premium quality. Different grades of PLC are used for high quality products such as pharmaceutical articles, light coloured and transparent goods, adhesives, tapes, tubing and derivatives such as chlorinated rubber. [10]

### Estate Brown Crepe (EBC)

These are prepared from cup lumps and other grades of scrap. Bark scrap can also be used after cleaning and removing the bark. Earth scrap and smoked scrap are not used for the production of EBC. [11]

### 1.2c Technically Specified Rubber (Block Rubber)

TSR is a modern form of marketable rubber and can be produced from latex, field coagulum or a blend of both. The production of TSR started only during the 1960s, prior to which raw natural rubber was marketed in conventional forms like sheet or crepe. NR marketed in ribbed smoked sheet (RSS) or crepe form, is graded only by visual standards. The inadequacies of the visual grading system became more obvious with the development of synthetic rubbers. [12]

### 1.2d Preserved Field Latex

A preservative is a chemical or mixture of chemicals which when added to latex can prevent bacterial action in it and at the same time stabilises it. Ammonia is the most popular latex preservative usually field latex is preserved with 1% ammonia. A low ammonia system consisting of TMTD and Zinc oxide (0.025% each) along with 0.35% ammonia is also popular.

Field latex preserved with suitable preservatives is termed as preserved field latex. Processing into preserved field latex consists essentially of adding the preservative, bulking, settling and blending into consignments of suitable size for despatch. The equipment required consists of latex reception tank and a few bulking tanks. The reception tank should be large enough to treat the whole crop. It is necessary to strain latex brought from the field and to mix calculated quantities of preservatives in it. If the magnesium content is abnormally high, diammonium hydrogen orthophosphate (DAHP) is added as a 10% solution, usually 5.5 times of the magnesium content.

After this, the latex is fed into a bulking tank and left undisturbed for a day. After removal of sediments, the latex is thoroughly but gently mixed. Samples are then drawn and tested for the preservative content and dry rubber content. Based on this necessary adjustments are made. The latex is then ready for packing and despatch as normal preserved field latex. [13]

## 1.2e Latex Concentrates

There is good market for preserved latex concentrates as it is an important raw material having wide uses. Two major methods of processing latex into preserved latex concentrates are commercially practised. They are briefly described below. [14]

### Concentration by creaming

The processing of latex into creamed concentrates involves the mixing of a creaming agent such as ammonium alginate or cooked tamarind seed powder with properly preserved field latex and allowing the latex to separate into two layers, an upper layer of concentrated latex and lower layer of serum containing very little rubber. The lower layer is removed, leaving the latex concentrates of 50% - 55% drc which is tested, packed and marketed. Though this method is very slow compared to the centrifugal method, it is still employed by small scale rubber goods manufactures for producing latex concentrate because of low investment. The specifications for creamed latex is described in IS 13101 : 1991.

## Concentration by Centrifuging

Centrifuging involves the separation of preserved field latex into two fractions, one containing the concentrated latex of more than 60% dry rubber and the other containing 4-6% dry rubber using a centrifuging machine. The rotating bowl of the centrifuge is fed continuously with preserved field latex which results in the continuous collection of concentrated latex that is drawn out through and outlet at the centre and the serum (Skim latex) near the circumference from where it is withdrawn through another outlet. The essential features of such a factory are a latex reception unit that acts as a feed reservoir for the centrifuge, the centrifuge itself with means of driving bulking and storage tanks, provision for packing in drums or tankers, means of preservation means for processing the skim and treatment plant for waste water. The skim is coagulated with sulphuric acid, creped, dried and marketed as skim rubber. This low grade rubber is not used in products requiring good service properties. [15]

## Properties of Natural Rubber

If we stretch a rubber band and release immediately, it takes almost its original shape and length. Similarly when a block is compressed and released the block will assume its original shape. These are requirements of "rubberiness". Another property of rubber is its strength and toughness. A very important quality of rubber is "building tack" i.e., when two fresh surface of milled rubber are pressed together, they coalesce to form a single piece. This makes relatively simple the building of a composite article such as tyre.

NR can be used in a large variety of applications. Major application of natural rubber is especially in the tyre sector. Also NR is used in the car cass as well as in the side wall due to fatigue superior resistance and low buildup. In commercial vehicles, the amount of NR increases with the size of the tyre. It is also applicable in mechanical goods, engineering products, lated goods and foot wear. [16]

## Visual Examination and Draw - backs of Visual Grading

Ribbed smoked sheets and crepe rubbers are graded and classified by visual comparison method. This provide ample room for mal practice. Besides, this unscientific system is not helpful to the consumer in assessing the quality of raw rubber. Synthetic rubbers are sold to manufactures in solid block form in attractive packing. Besides, the grading of synthetic rubber is done by technical specification. So in order to strengthen the competitive base of natural rubber it become necessary to give it an appearance, presentation and grading comparable to those of synthetic rubber. Processing of natural rubber in technically specified block form was evolved in this context. [17]

## 1.3 Development of SMR Scheme in Malaysia

### 1.3a Introduction of Scheme

The natural rubber industry first introduced technical tests for NR in 1950 (RUBBER RESEARCH INSTITUTE OF MALAYA, 1952) in the form the T.C. scheme which classified rubbers according to the rate of vulcanizations but relies on visual grading methods for other properties; some 29870 tons of NR were classified under this scheme in Malaysia in 1967.

The introduction of new presentation processes for NR soon necessitated other technical specifications for block rubbers. Their application to conventional grades was also desirable. The SMR scheme was therefore evolved for general-purpose Malaysian NR in conventional and new forms, the latter being presented in small bales, wrapped in polythene or other approved material, and free from bale coatings. A survey of producers' capabilities, consumers requirements and properties of existing market grades together with an overall desire for simplification led to the choice of three grades of Standard Malaysian Rubber (RUBBER RESEARCH INSTITUTE OF MALAYA, 1965). The properties of SMR varieties are shown in Table -III

## Table - III

## MAXIMUM PERMITTED CONTENT OF CONSTITUENTS IN SMR

| Constituent | SMR 5 | SMR 20 | SMR 50 |
|---|---|---|---|
| Dirt , % wt | 0.05 | 0.20 | 0.50 |
| Ash, % wt | 0.5 | 1.0 | 1.5 |
| Copper, p.p.m | 8 | 8 | 8 |
| Manganese, p.p.m | 10 | 10 | 20 |
| Nitrogen, % wt | 0.7 | 0.7 | 0.7 |
| Volatile matter, % wt | 1.0 | 1.0 | 1.0 |

In addition, a new test for oxidisability known as PRI was used to ‘Screen’ rubbers for these grades.

These properties were initially considered essential for launching the scheme and, as more information and experience became available. It was intended to eliminate tests which were proved redundant or add other tests which were shown to be necessary. The properties specified would not exclude other properties (e.g. TC strain) which could be agreed to between the producer and the consumer, outside the SMR scheme.

### 1.3b Operation of Scheme

Several important steps were taken to ensure consumer confidence in the scheme. These included the following.

i. The production of SMR was permitted only after registration of the producer by the Malayan Rubber Export Registration Board, which acted on technical advice from R.R.I.M.

ii. Punitive action (including deregistration) could be taken against a producer who did not conform to the requirements of the scheme; and

iii. The conformance guarantee allowed the rejection of any bale of rubber found to be outside the specification and the rejection of any consignment if the mean of 10% of the bales were found to be outside the specification.

To enable such a guarantee to be given with confidence, statistical methods were applied to the test results obtained from all production lots, e.g. to guarantee a dirt content of less than 0.05% (SMR 5). Ten percent of the bales in the lot were tested individually and the sum of mean plus three times the standard deviation of these samples was required to be less than 0.05%. The collection of several lots into one consignment would not alter the bale or consignment guarantee but this statistical system of evaluation could not then be applied to the consignment as a whole.

This system of operation enabled producers to reduce variability to the minimum. In routine large-scale production, the mean value of dirt content rarely exceeded two-thirds of the maximum specification value. Such methods were initially considered almost penal by the producers but further experience and demonstrations of the methods have now convinced most producers that the system is a reasonable one. It is possible to introduce more simple modifications of this statistical system in day-to-day regular production, but such systems must not be less discriminating than the initial scheme which is always applied in full for new factories starting production.

### 1.3c Success of Scheme

Many consumers tested early deliveries carefully and extensively and expressed considerable surprise and pleasure at finding all properties well within the range specified in the SMR scheme, even when separate bale samples were checked. In the case of SMR 5L, the mean dirt content is often less than 10% of the maximum permitted value. These results have revived consumers' interest in NR because they are in sharp contrast to the long prevalent practice of grading conventional rubbers according to the port, price and inspection procedure. This practice is regretted by both producers and consumers but is inevitable under competitive marketing procedures. Only the SMR scheme offers the solution to this problem.

Unfortunately, some deliveries of SMR have been found to be unsatisfactory. Some complaints were due to the inexperience of new producers and action has been taken to remedy the drawbacks in existing factories; in addition, the R.R.I.M. has started a processing instructors' course to train factory operators and advisory personnel on how to prevent substandard production in new factories. Most causes of complaints have, however, been due to factors outside the control of the NR producers: contamination in ships' holds or wetness due to exposure of the rubber to rain during storage or carriage in consuming countries. Efforts to reduce such contamination should continue vigorously at least until containerisation becomes the accepted means of transport.

Bale and pallet packing have also been improved. Initial complaints made on the basis of high dirt content were unjustified, often being the result of faulty analytical determination by consumers or adventitious contamination in transit and storage. As a further safeguard to the integrity of the SMR scheme, the R.R.I.M intends to establish an Inspectorate whose personnel will be entitled to sample and test production or shipments to detect any abuse of the scheme.

It should also be emphasized that complaints have been few, and almost all consumers have been enthusiastic about SMR deliveries; this is reflected in the rapid increase of SMR output. [18]

## 1.4 Review of Literature

Consumers have indicated a desire for more 'rubber' tests such as cure rate, modulus or tensile strength, viscosity or plasticity, and PRI.

The request for some vulcanisate tests is not universal since consumers using certain accelerators claim that cure rate is no problem. Investigations are still under way on the evolution of a suitable and meaningful test of value of consumers. It is expected that such a test would indicate a typical or average value for the consignment.

Viscosity of a rubber can be guaranteed only if it has been specifically stabilized as in the production of Heveacrumb CV. This rubber is already on the market and has proved to be very popular.

Much work has been carried out on the PRI test (BATEMAN AND SEKHAR - 1966) since the SMR scheme was introduced, and its value is now generally accepted. PRI is more sensitive than a copper test to indicate contamination or possible degradation due to this metal. Further, the effect of large quantities of manganese have been shown again to be relatively harmless. It therefore seems logical to remove the complicated and expensive copper and manganese tests, when the simple PRI test is introduced.

Although a large number of processes could be devised from the variables covered in this review, the choice should be made with the following basic aims.

1. To obtain a product of satisfactory technical properties, classifiable in the SMR scheme.
2. To be economical in operation; and
3. To be sufficiently flexible to handle all raw materials available and the likely future products under development.

If these objects are realised, the processing system chosen is satisfactory. The resulting rubbers classified under the SMR scheme assure consumers standards of quality and presentation which should meet their increasingly discriminating requirements. [19]

## 1.5 DEVELOPMENT OF ISNR SCHEME IN INDIA

Developments in industrial techniques necessitate that natural rubber producers must be able to guarantee the consistency in quality of the rubber. Attempts have been made in India and other rubber producing countries for standardization of the processing techniques and development of improved machinery. So that TSR of better quality could consistently be produced.

Introduction of a slab cutter or pre-breaker in the initial size reduction stage, use of macro-and micro blending tanks, transfer of raw materials from one tank to another while under motion by bucket elevator system and loading of final crumbs to the drier boxes with a solids pump, through a vibrating perforated screens and hopper, are some of the modern developments in TSR processing. They bales can be passed through a conveyor fitted with a metal detecting device at the end of which an LDPE bag is introduced on a side frame for easy wrapping of the block.

Use of latex coagulum along with field coagulum, in suitable blends, is also aimed at improving quality. The present trend in the design of a TSR factory in India is to include improved blending facilities so that block rubber of different grades and specifications could be produced as per customer requirements.

## Specifications and Grading

The International standards organization (ISO) formulated draft specifications for NR in 1964 and the important parameters included were dirt content, volatile matter, ash, nitrogen, copper, manganese. In line with these standards, Malaysia introduced technical specifications for TSR (block rubber) under the title SMR specifications. In 1970, these specifications were revised introducing PRI in place of copper and manganese. Further revisions were carried out from time to time according to the requirements of the consuming sector.

In 1968, the Indian standards institution introduced technical specifications for three grades of NR as grade - A, grade- B, grade- C in line with the draft standards made by ISO. With the commercial production of block rubber in the country in 1973 and based on consumer preference the ISI revised these three grades into five grades of Indian standard Natural Rubber (ISNR) . They were ISNR 5 special, ISNR 5, ISNR 10, ISNR 20 and ISNR 50. These grades and their specifications were subsequently revised according to the requirements of NR consuming industry in 1975, 1977, 1986 and 1992. In the meantime, ISNR 5 special was replaced, and ISNR 3L and ISNR 3 CV (a constant viscosity version) were introduced.

At present, there are six grades of TSR processed and marketed in India of which ISNR 3L and ISNR 3CV are produced from latex, while ISNR 5 is produced either from latex, grade or high quality coagulum grade rubber. ISNR 10, ISNR 20 and ISNR 50 are processed from field coagulum grades or a blend of latex and field coagulum grades.

The bureau of Indian Standard (BIS) revised technical specifications of TSR based on consumer requirements, producer capabilities and technology developments around the world.

The specifications as per the latest revisions adopted by American society for testing and materials (ASTM) and BIS are given in Tables IV and V respectively.

## **Specification for NR technical grades.**

Table IV ASTM specifications of block rubber

| Property | Rubber Grade | | | | |
|---|---|---|---|---|---|
| | L | CV | 5 | 10 | 20 |
| Dirt retained on 45 micron sieve (% Max) | 0.05 | 0.05 | 0.05 | 0.10 | 0.20 |
| Ash (% Max) | 0.60 | 0.60 | 0.60 | 0.75 | 1.00 |
| Nitrogen (% Max) | 0.60 | 0.60 | 0.60 | 0.60 | 0.60 |
| Volatile matter, (% Max ) | 0.80 | 0.80 | 0.80 | 0.80 | 0.80 |
| Initial Plasticity , $P_0$ (Min) | 30 | - | 30 | 30 | 30 |
| Plasticity Retention Index, PRI (% Min) | 60 | 60 | 60 | 50 | 40 |
| Colour (Lovibond scale, Max) | 6.0 | - | - | - | - |
| Mooney Viscosity ML (1+4) 100°C | - | 60±5 | - | - | - |

## Table - V

## Indian Standard Specification for raw natural rubber

| Characteristic | ISNR 3CV | ISNR 3L | ISNR 5 | ISNR 10 | ISNR 20 | ISNR 50 |
|---|---|---|---|---|---|---|
| Dirt retained on 44 micron aperture (% Max) | 0.03 | 0.03 | 0.05 | 0.10 | 0.20 | 0.50 |
| Ash (%Max) | 0.50 | 0.50 | 0.60 | 0.75 | 1.00 | 1.50 |
| Nitrogen (% Max) | 0.60 | 0.60 | 0.60 | 0.60 | 0.60 | 0.60 |
| Volatile matter (% Max) | 0.80 | 0.80 | 0.80 | 0.80 | 0.80 | 0.80 |
| Initial plasticity, $P_0$ (Min) | * | 30 | 30 | 30 | 30 | 30 |
| PRI (Min) | 60 | 60 | 60 | 50 | 40 | 30 |
| Colour (Lovibond Scale,Max) | - | 6.0 | - | - | - | - |
| Mooney Viscosity ML (1+4) at $100^0$C | $60 \pm 5$ | - | - | - | - | - |
| Accelerated storage hardening (Max) | 8 | - | - | - | - | - |
| Colour code | Light green | White | Green | Brown | Red | Yellow |

* As agreed by the purchaser and supplier

The specifications and standards are formulated to meet the ultimate consumer requirements and demands which may be broadly categorized as follows.

## Purity

This is perhaps more relevant to increased productivity in factories adopting modern extrusion technology. Flex resistance and tensile strength are the properties most adversely affected by the presence of higher dirt content. It also leads to development of flaws in the final product.

## Contamination

TSR should not be contaminated with extraneous materials such as jute/poly propylene strings, semi-vulcanized compound rejects or wet spots. It may possibly give rise to poor mixing and poor vulcanizate properties.

## Consistency in processability

Consistency in processability is not definable in a universally acceptable manner. The parameters which indicate this are initial plasticity ($P_0$) and plasticity retention index (PRI), based on consumer requirements.

## Physical Properties

The physical properties of TSR are generally more than adequate to meet the manufacturing and product quality requirements. Dirt, $P_0$ and PRI provide a good indication of the physical properties to be expected. However, automated processing and computer controller machinery in product manufacture necessitate more information in viscosity, physicochemical properties and rheological properties of the raw material. The critical properties of the raw material which are to be controlled for producing TSR of consistent quality have been identified by Baker and Bristow (1991)

## Packaging

The inner packaging should be with LDPE film having melting point less than 110$^0$C for proper miscibility with rubber at the time of mixing.

## Quality system

Adoption of TQM/ISO 9000 quality system is an imperative need of the hour. All the TSR producers shall evolve and maintain a quality assurance system to satisfy their consumers. For this, strict control on basic raw material and production process is to be effected.

## Regular Supply

Regular and assured supply of consistent quality raw material is a basic requirement to save on inventory cost for product manufacturing units and hence this aspect is economically very significant.

## Advantages of TSR

Advantages of TSR are assurance of quality with respect to important technical parameters consistency in quality, clean and easy to handle packing, minimum storage space and reduction in processing time.

Consistency in quality can be achieved by inbuilt process control systems and standardization of the processing methods. The development of this process technology has helped the rubber plantation industry to improve the competitive position of NR by improving the output and productivity from the processing unit and introducing more efficient processing methods to meet the consumer requirements. Production of TSR takes only a shorter time than that of conventional grades like sheet or crepe and the product is very easy to handle and store. The consistent and specified properties of TSR make it far more attractive to the consumers.

## The main advantages of TSR are that

1. · It is available in six different grades with technical specifications and consumers can choose the grades according to requirement,

2. As it is processed in bulk quantities adopting latest technology, variations in properties within the same grade is minimum
3. Impurities in the rubber can be assessed as the content of foreign material and volatile matter, and
4. Being marketed in compact poly ethylene wrapped bales, contamination on storage handling and transportation is avoided. Moreover, the use of TSR gives significant improvement in processing behavior, uniform product quality and reduction in rejects. [20]

## Grades

### ISNR 3CV

This grade is produced from good quality field latex and is viscosity stabilized at a narrow range (60±5). This is mainly used in the manufacture of tyres, engineering components, extruded and calendered products, etc. where physical properties of the final product are very critical and consistency in processing behaviour is highly desirable.

### ISNR 3L

This grade is also produced from good quality field latex and the maximum colour of this rubber as per the lovibond scale shall be six units. ISNR 3L is mainly used for light coloured products, pharmaceutical products, feeding bottle, teats and large industrial rollers for paper and printing industry, which require high purity. It is a possible substitute for pale latex crepe.

### ISNR 5

This is processed using field latex or high quality field coagulum as the main raw material and is widely used in the manufacture of high quality products like conveyor belts, cycle tubes, engine mountings, footwear etc. ISNR 5 is a possible alternative to higher quality sheets.

## ISNR 10, ISNR 20 AND ISNR 50

These grades of TSR are processed from quality field coagulum material and can be used for the manufacture of rubber products according to the quality requirements in place of conventional lower grades of sheet rubber and crepe. Generally, ISNR 10 and ISNR 20 grades are used by tyre manufactures in bulk. ISNR 50 grade is used for the production of cheap products like handmade hose, footwear, mats and moulded goods. [21]

## Trends in India

In the major rubber producing countries like Thailand, Indonesia and Malaysia, substantial quantities of NR are produced in the form of TSR. In Indonesia and Malaysia the TSR production is more than 70 percent and in Thailand it is about 17 percent of the total production. The capacity of TSR factories in these countries is comparatively high, ranging from 40 to 100 per day. The factories are becoming more and more automated and mechanized.

In India, conventional forms such as sheet and crepe still account for the major portion of processed rubber only about ten percent of the total rubber produced is processed as TSR. The factories are comparatively small and capacity utilization is poor. The main reason for this situation is that in India TSR is produced mostly from field coagulum. The total quantity of field coagulum is 20 to 30 percent and a part of this is processed as crepe as well. Production of latex grade TSR is very limited due to economic and commercial factors and the predominance of small holders who prefer to sell their corps as RSS. Adoption of the following steps will be beneficial for improving the TSR situation in India.

* Collection and processing of raw material (field coagulum) without degradation and preferably as fresh scrap. If this is not practicable, blending with latex coagula is to be carried out.

- Proper storage and handling of raw material at the factory preliminary quality control to be adopted to assess the quality of raw material.
- Use of improved machinery like pre-breaker/slab cutter for size reduction.
- Providing blending tanks for better homogenization and to avoid variations in raw material.
- Implementation of TQM in the factories.

## 1.6 Processing of Technically specified Rubber

Technically specified rubbers are largely block types made by adopting new methods of processing. All new methods of processing thus evolved can handle coagulum produced from latex and all forms of scarp rubber and involved practically the same unit operation which are given below.

1. Initial size reduction
2. Creping
3. De-Watering
4. Final size reduction
5. Drying
6. Bailing
7. Grading

### 1.6a Initial Size reduction, de-watering and creping

In all the new processes usually these three operations are accomplished together. A variety of machines which cam disintegrate the coagulum or scarp into granules, pellet or crumbs and at the same time able to remove water to considerable extent can be used for this purpose. Machineries used for initial size reduction are slab cutter, pre breaker and hammer mill. For creping crepers or macerators are used.

### 1.6b Final Size Reduction

The different items of machinery used for the final processing of the pre-cleaned material for TSR production are creper-hammer mill, shredder and extruder.

## 1.6c Drying

Drying is carried out at about 100$^{0}$C. Drying time depends upon the size of the particles usually 4 to 5 hours are required for complete drying. The tunnel drier is commonly used.

## 1.6d Bailing, grading and packing

The dried crumbs, pellets or granules are pressed when they are below 50$^{0}$C in a hydraulic press. 30 to 50 tonne pressure is generally used. Bales preferably 25 kg are generally prepared. Samples are then cut from a few representative bales and tests for technical specification are undertaken. The following tests are usually done.

1. Dirt Content
2. Ash content
3. Volatile matter
4. Nitrogen content
5. Initial Wallace Plasticity
6. Plasticity retention Index
7. Colour
8. Mooney Viscosity
9. Accelerated storage Hardening Test

Based on the test results, grading is done. The bale are then wrapped in polythene films, packed in HDPE bags and marketed. [22]

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# CHAPTER II

# EXPERIMENTAL METHODS

## 2.1 TEST OF NATURAL RUBBER

### 2.1a Homogenisation of Test Piece

In order to make the sample portion more uniform, it is passed six times through the gap between the rolls of a laboratory mill at a nip setting of 1.65 ± 0.15 mm and at room temperature. Due to shearing action of rubber the mills are heated up. The rolls are cooled to room temperature by running water. After each pass the rubber is rolled into a cylinder and introduced end wise for the next pass. The rubber is not rolled after the fifth pass.

Portions of following approximate weights are cut from the blended piece for various tests.

**Table - I**

| Test | Quantity (gm) |
|---|---|
| Dirt | 25 - 30 |
| Volatile Matter | 25 - 30 |
| $P_0$ and PRI | 25 - 30 |
| Colour | 20 |
| Mooney Viscosity | 50 |
| Ash & Nitrogen | 20 |

The portion for volatile matter determination is wrapped in a polythene bag to prevent exchange of moisture with the atmosphere.

### 2.1b Test Piece Cutter

The special Test Piece Cutter provided is designed to cut test pieces of approximate constant volume from slabs of material of varying thickness. The cutter is designed to receive material from 3mm, 8mm, thick. It will be found advisable to secure the cutter to the bench, preferably with the cutter anvil projecting beyond the bench for easier adjusting.

## Description (See Diagram on following page)

A circular plunger (Cutter Guide A) compresses the material to a definite thickness before the cutter (Cutting Knife B) cuts out the specimen. The cutting edge beds down on a soft aluminimum washer (Soft Washer C) to prevent damage.

## Adjusting the Cutter

When supplied, the test piece cutter will be correctly adjusted. However, the cutter should be checked and adjusted once a week as follows :-

All adjustments should be made with all play in the cutter taken up.

1. The whole circular blade of the cutting knife should just make contact with the soft washer when the cutter is closed.

   To adjust :- Close the cutter, slacken locking screw (D)

   Turn the cutter anvil (E) to achieve the correct setting.

   Tighten locking screw and re-check the setting.

   After some considerable use the soft metal washer will become worn and should be replaced.

   To replace :- Slacken locking screw (D). Remove the cutter anvil (E) from the test piece cutter and replace the soft metal washer. (Located by a counter-sunk screw (J) in the centre). Re-fit the cutter anvil and adjust as above.

2. With the blade of the cutting knife level with the flat face of the cutter guide, the gap between the soft washer and the cutter guide should be 3mm.

To adjust :- Slacken Nut (F). Turn Hollow Screw (G) to obtain correct setting. Retighten Nut (F) taking care not to disturb the setting.

3. The Screw (H) keeps the Cutter Guide in position. This should be tight in the Cutter Guide but there should be aproximately 0.25mm end float in the Hollow Screw (G)

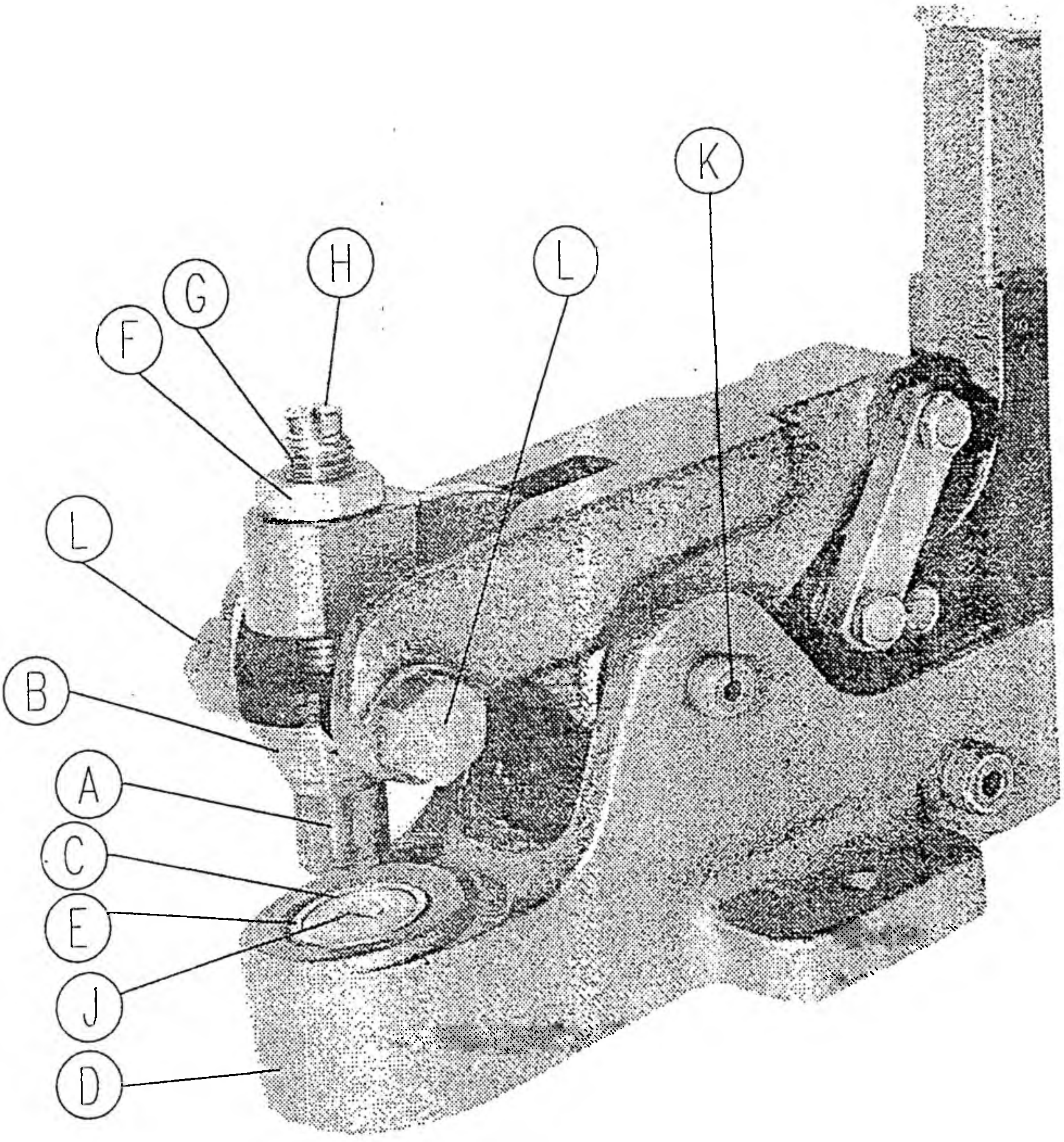
4. After some considerable use the Cutting Knife (B) may become worn or damaged. The Cutting Knife can then be replaced.

   To replace :- Remove bolts H and L, LIft out cutter and cutter guide.

   Fit a new Cutting knife. Replace Pivot Bolt (K) and re-check setting of cutter as in 1,2 and 3 above.

## General

Regular checking and adjustment of Test Piece Cutter will be repaid by improved consistency in Plastimeter readings.



TEST PIECE SPECIMEN CUTTER

## Compression Plastimeters

A small cylinder of the rubber is compressed between paralled plates under a definite force for a definite time normally at elevated temperature, the compressed thickness being the plasticity number. Such tests are simple and quick, bu shear rates produced are very low. There are basically two forms of paralled plate compression testers.

1. William Plastimeter (Plate test) and
2. Wallace rapid plastimeter

In the Wallace Rapid Plastimeter, the test piece is precompressed to 1mm thickness and preheated to 100$^0$C for ten seconds. The compressive force (10 kg) is then applied for 15 seconds, so that the test is completed in less than a minute. The test result is the thickness in mm/100 and is the rapid plasticity number. A high plasticity number denotes a soft rubber. This test has been widely adopted for the determination of the plasticity retention index (PRI) of raw rubbers.

## 2.2 Testing of Raw Rubber for Initial Plasticity ($P_0$) and Plasticity Retention Index (PRI)

The Plasticity Retention Index (PRI) test has been developed as a simple method for measuring the resistance of raw rubber to oxidative break down on heating.

## 2.2a Principle

A disc shaped test piece is rapidly compressed between small parallel platens to a fixed thickness of 1mm and hold them for 15 second to enable the test piece to reach approximate temperature equilibrium with the platens. It is then subjected to a constant compressive force for 15 seconds. Its thickness at the end of the period expressed in 0.01mm units is taken as plasticity. Plasticity retained after ageing in an oven for 30 ± 0.25 minutes at 140$^0$ C is measured with plastimeter. The PRI is then calculated as the percentage ratio of plasticities before and after heating.

## 2.2b Procedure

Calibrate the plastimeter according to the direction given.

A test portion of 20 g of the homogenized piece is passed twice through the rolls of a cool mill with nip setting adjusted such that the final sheet thickness is 1.6-1.8mm. The sheet free from hole is immediately double and the two halves pressed lightly together by hand. Six pellets are cut from the doubled sheet with the punch. The test piece should be disc of rubber at thickness between 3.2-3.6mm and approximately 13mm in diameter.

## 2.2c Ageing

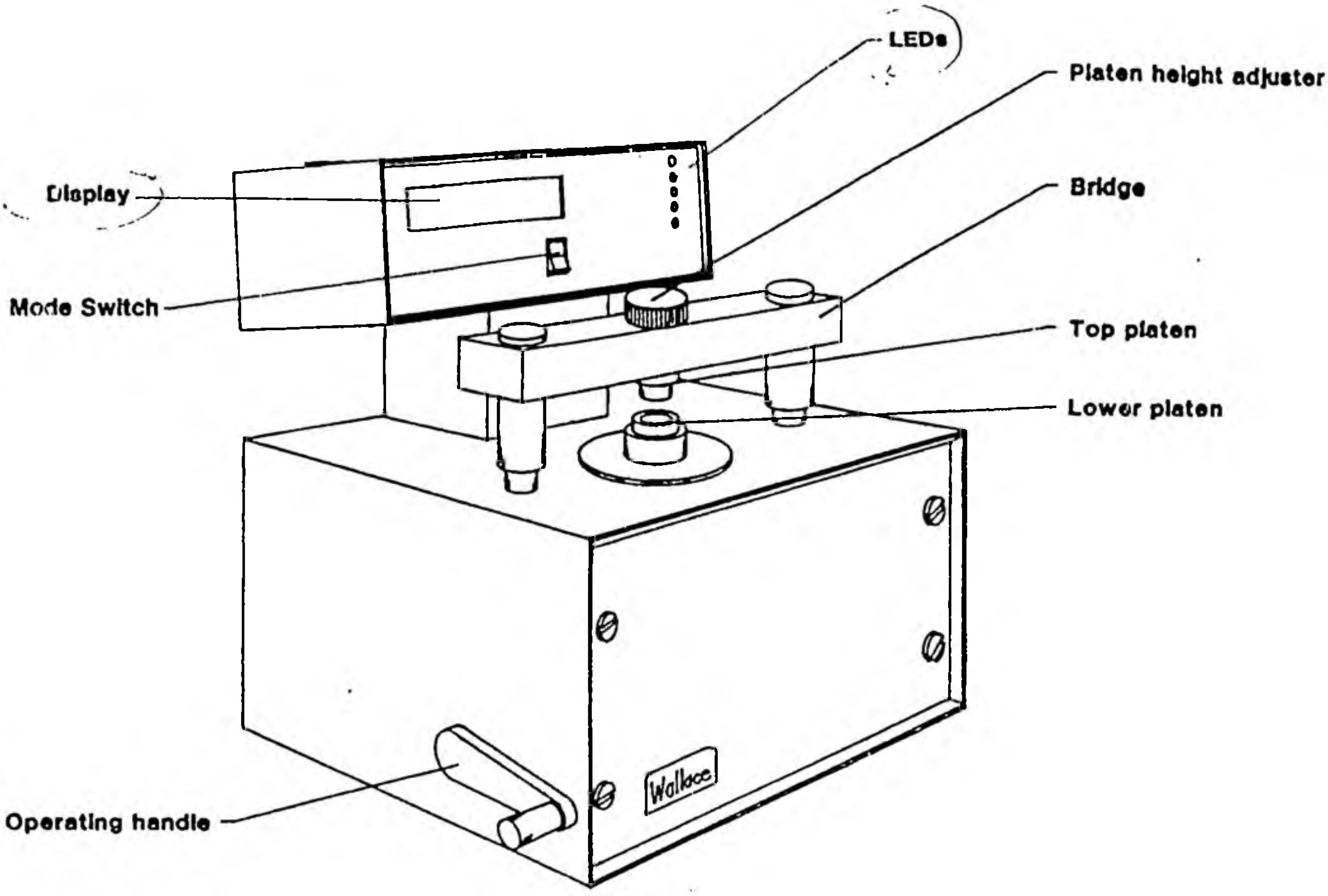
The ageing oven is adjusted to 140+/- 0.2$^0$C. The sample pellets arranged in the aluminium trays are inserted quickly into the oven the timing started. After 30 $\pm$ 0.25 minutes the tray is removed from oven and allowed to cool to room temperature.

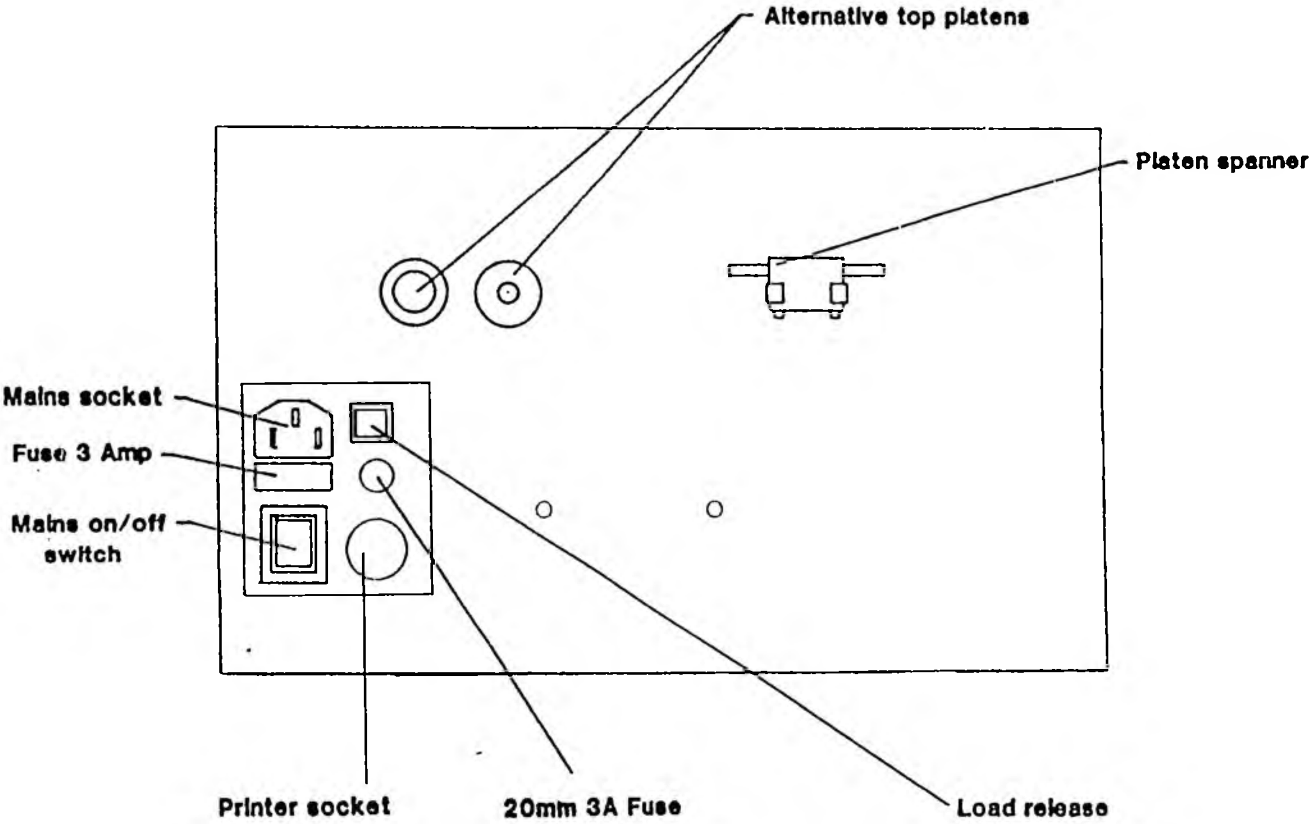
## 2.2d Measurement of Rapid Plasticity

Each pellet sand wiched between two pieces of cigarette paper each of dimensions 40 x 35 mm is compressed between the two parallel platens to a fixed thickness of 1mm and held for 15 seconds to reach approximate equilibrium with the platen temperature. It is then subjected to a constant compressive force of 10 +/- 0.1 kg for 15 seconds. Thickness of the sample piece at the end of this period (in 0.01 units) is taken as the measure of rapid plasticity. The values for an pellets is noted as initial plasticity $P_0$ and aged sample as $P_{30}$

## 2.2e Calculation

$$\text{PRI} = \frac{\text{Aged median Plasticiy Value x 100}}{\text{Initial median plasticity Value}}$$ [23]





View of back panel

Fig - 5

## 2.3 Significance of $P_0$ testing

Initial wallace plasticity ($P_0$) is a measure of the plasticity of the rubber which indirectly gives the estimation of the polymer molecular chain length (or molecular weight) . In general rubber with high $P_0$ values would possess high molecular weight. The specification limit of $P_0$ 30 for all SMR (with the exception of viscosity stabilised grades), ensures that the rubbers have a certain minimum molecular weight (weight average molecular weight = 1300000). SMR (with the exception mentioned above) with low $P_0$ values are normally associated with rubbers whose molecular chains have been degraded or undergone extensive chain-scissions, which are noted to have poorer technological properties. [24]

## 2.4 Significance of PRI testing

The Plasticity Retention Index was developed as a simple, rapid method of measuring the resistance of raw rubber to oxidation. Oxidation in rubber is always accompanied by molecular degradation or chain scissions. The PRI test is based on the retention in the plasticity of the rubber after oven aged at 140°C for 30 minutes.

The standard ageing conditions agreed after consultation with the rubber research institute of Malaysia are 30 minute at 140°C. The reasons behind this choice are that the change in plasticity is a typical first order process and therefore that PRI is a true characteristic of a rubber sample, unaffected by extent of oxidation, and that at temperatures below 130°C some rubbers can show an initial increase in plasticity. Temperature above 140°C were considered but problems of temperature control were considerable and with the necessary short ageing times the time to obtain temperature equilibrium becomes a significant proportion of the ageing time and an additional cause of error.

Considerable work was carried out to ascertain the major sources of error in the complete test. By far the most likely was found to be the temperature of ageing followed by the sample thickness and the temperature of the plasticity pattern. The last two sources affect both the before and after values of the plasticity and thus have a less serious effect on the actual PRI value.

PRI is expressed as the percentage of the plasticity after ageing to the plasticity before ageing of similar specimens.

$$\mathbf{PRI} = \frac{\mathbf{P_{30}}}{\mathbf{P_0}} \times 100$$

Where $P_{30}$ - Wallace plasticity of sample after ageing at 140$^0$C for 30 minutes.

$P_0$ - Initial wallace plasticity.

It is noted that low PRI value is associated with low $p_{30}$ and high $P_0$ values. Very low $p_{30}$ value compared to $P_0$ is obtained if the rubber is less resistance to oxidation resulting in severe chain - scission. Thus a low PRI value indicates molecular breakdown on ageing. Besides, it also provide a quantitative indication of the inherent quality of the rubber, its processing behaviour and derived vulcanisable properties.[25]

••••••••••••••••••••••••••••

# CHAPTER - III

# EFFECT OF OXALIC ACID ON PRI OF BLOCK NATURAL RUBBER

## 3.1 Materials Used

Field coagulum used for experimental purpose was received from pilet crumb rubber factory (PCRF) in Rubber Research Institute of India, Kottayam.

## 3.2 Chemicals Used

Oxalic Acid, sodium Oxalate and Potassium Oxalate

## 3.3 Effect of Concentration of Oxalic Acid on PRI of raw natural rubber

Prepared 0.025%, 0.05% and 0.1% oxalic acid solution. Soak about 100g of the sample in each of the solution for 30min. The sample is then dried at $100^0$ C and $P_0$ and PRI were found out.

Fresh samples were soaked in 0.1%, 0.2% and 0.4% oxalic acid. As above $P_0$ and PRI of the samples were determined.

## 3.4 Effect of duration of soaking in oxalic acid on changes in PRI

$P_0$ and PRI of the sample were found out using 0.1% oxalic acid by changing the duration of soaking. That is 10min, 20min and 30 min.

The same procedure is repeated for a number of samples.

## 3.5 Effect of addition of oxalic acid in various chemical forms

$P_0$ and PRI of the sample were found out using sodium oxalate and potassium oxalate. For this prepared 0.1%, 0.2% and 0.4% solutions of sodium oxalate and potassium oxalate. Soak about 100g of the samples in each solution. Then $P_0$ and PRI were found out.

In each of the above cases $P_0$ and PRI of the control were also found out. The results obtained are shown in chapter IV.

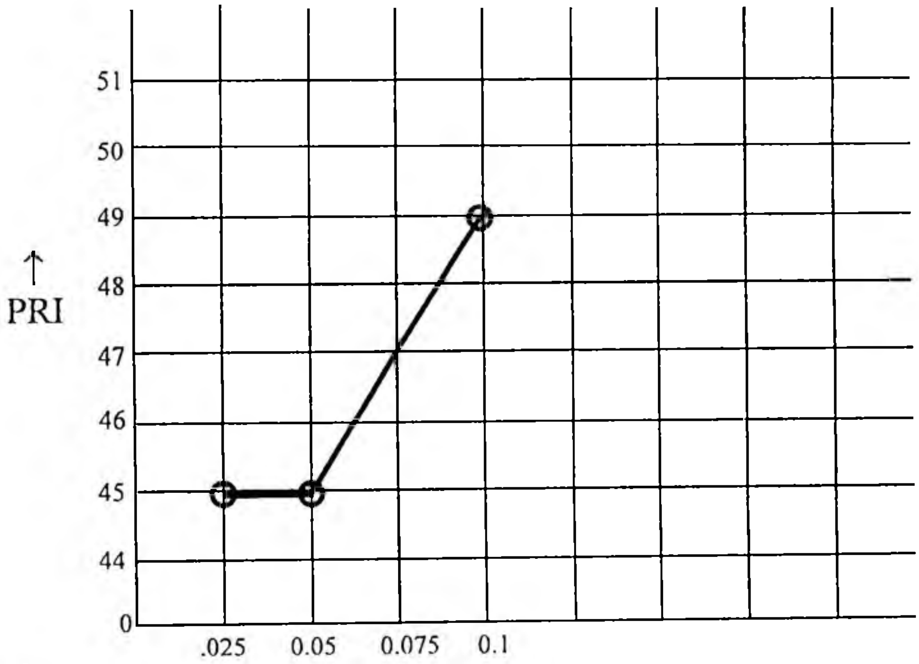
# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 Effect of Concentration of Oxalic Acid on Plasticity Retention Index (PRI) of Raw Natural Rubber

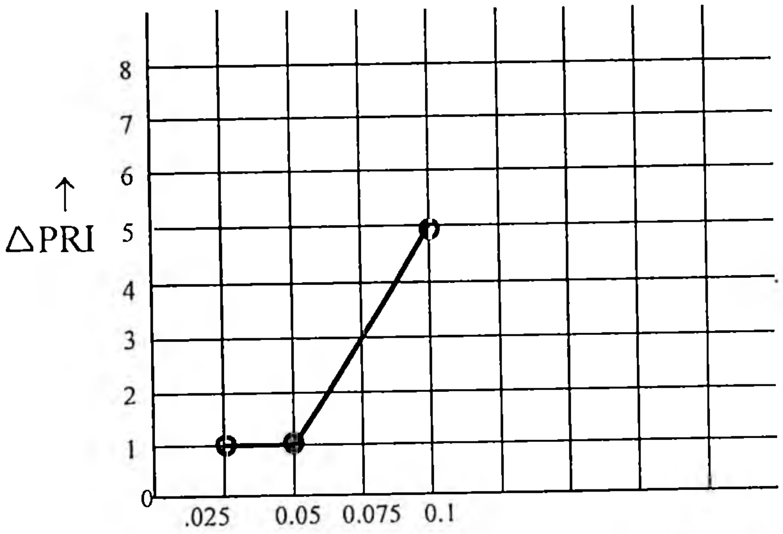
### 4.1a Concentration upto 0.1%

| Additive | 0.025% | | 0.05% | | 0.1% | |
|---|---|---|---|---|---|---|
| | $P_0$ | PRI | $P_0$ | PRI | $P_0$ | PRI |
| Control | 50 | 44 | 50 | 44 | 50 | 44 |
| Oxalic acid | 47 | 45 | 47 | 45 | 45 | 49 |



Concentration of Oxalic Acid →

| Additive | 0.025% | 0.05% | 0.1% |
|---|---|---|---|
| ΔPRI | +1 | +1 | +5 |



Concentration of Oxalic Acid →

Where ΔPRI is the difference in plasticity between the control and the soaked sample.

The Results are shown in table. From the graph it is clear that there is pratically no change in PRI when the concentration of oxalic acid is upto 0.05%. But there is a marked increase in PRI when the concentration of oxalic acid is 0.1%. Hence higher concentrations of oxalic acid also were tried.

## 4.1b Concentration from 0.1% to 0.4%

| Additive | 0.1% | | 0.2% | | 0.4% | |
|---|---|---|---|---|---|---|
| | $P_0$ | PRI | $P_0$ | PRI | $P_0$ | PRI |
| Control | 58 | 48 | 58 | 48 | 58 | 48 |
| Oxalic acid | 55 | 56 | 56 | 59 | 59 | 61 |

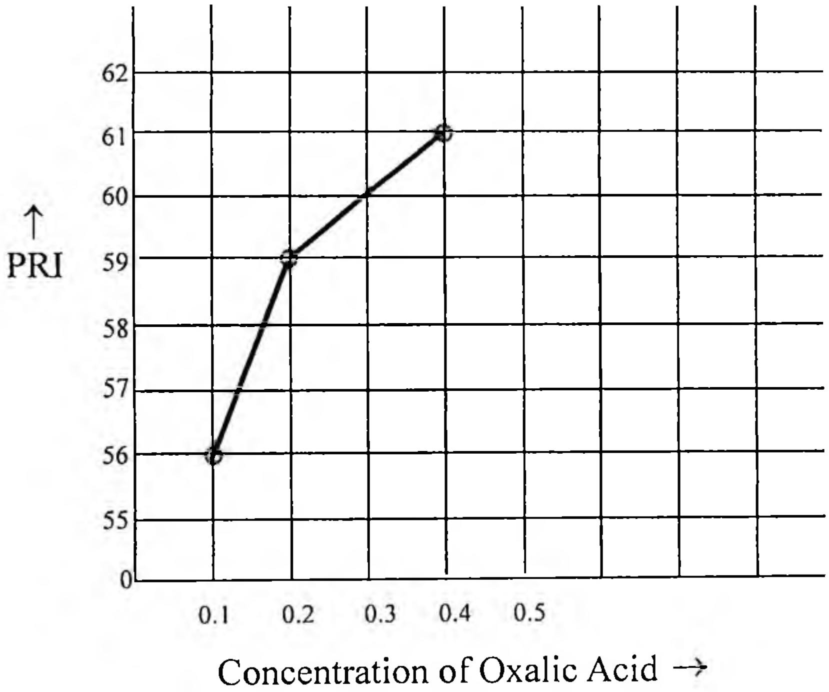
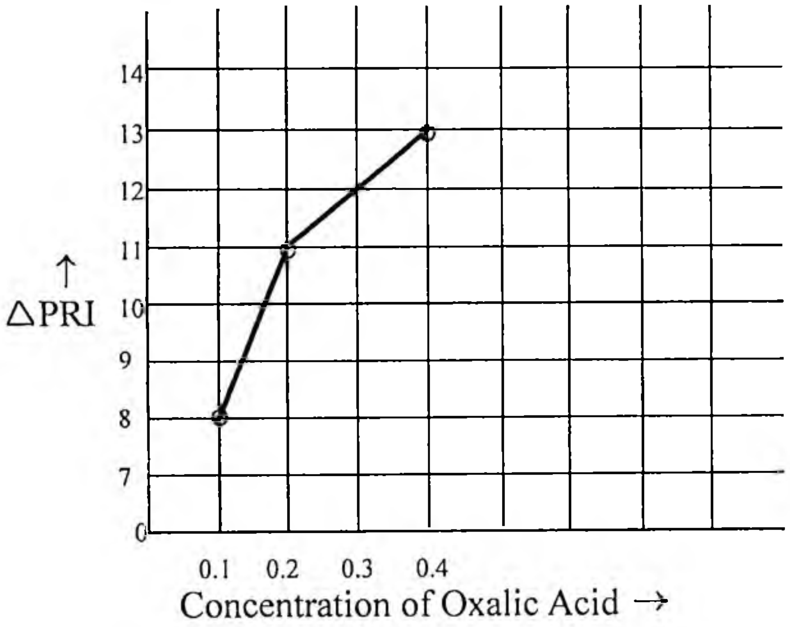


**Table IV**

| Additive | 0.1% | 0.2% | 0.4% |
|---|---|---|---|
| | Δ PRI | Δ PRI | Δ PRI |
| Oxalic Acid | +8 | +11 | +13 |



The results obtained are shown in figure. From the graphs it is clear that, on increasing the concentration of oxalic acid from 0.1% onwards PRI of rubber sample increases; however the increase is only nominal over 0.1%. Hence it was concluded that oxalic acid concentration of 0.1% was the optimum. Further studies were conducted at 0.1% concentration.

PRI of rubber is decided to a great extent by the presence of pro-oxidant metallic ions in rubber. Major pro-oxidants are ions of copper, manganese and iron. It is believed that these metals are effectively complexed by oxalic acid forming undissociated oxalate complex. This reaction deactivates these metallic ions from functioning as prooxidants.

$$M^{+n} + \frac{n}{2}\, C_2O_4^{-2} \longrightarrow M(C_2O_4)_{n/2}$$

The rubber is thus indirectly protected to a certain extent from thermo oxidation degradation, as shown by increase in PRI values.

## 4.2 Effect of Duration of Soaking in Oxalic Acid on Changes in PRI

### Sample I

| | 10 min | | | 20 min | | | 30 min | | |
|---|---|---|---|---|---|---|---|---|---|
| | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI |
| Control | 52 | 27 | 52 | 52 | 27 | 52 | 52 | 27 | 52 |
| 0.1% oxalic acid | 49 | 28 | 57 | 47 | 27 | 57 | 50 | 28 | 56 |

### Sample II

| | 10 min | | | 20 min | | | 30 min | | |
|---|---|---|---|---|---|---|---|---|---|
| | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI |
| Control | 48 | 26 | 54 | 48 | 26 | 54 | 48 | 26 | 54 |
| 0.1% oxalic acids | 46 | 26 | 57 | 46 | 26 | 57 | 48 | 28 | 58 |

### Sample III

| | 10 min | | | 20 min | | | 30 min | | |
|---|---|---|---|---|---|---|---|---|---|
| | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI |
| Control | 47 | 25 | 53 | 47 | 25 | 53 | 47 | 25 | 53 |
| 0.1% oxalic acid | 44 | 26 | 59 | 45 | 26 | 58 | 45 | 26 | 58 |

## Sample IV

| | 10 min | | | 20 min | | | 30 min | | |
|---|---|---|---|---|---|---|---|---|---|
| | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI |
| Control | 47 | 17 | 36 | 47 | 17 | 36 | 47 | 17 | 36 |
| 0.1% oxalic acid | 47 | 21 | 45 | 48 | 21 | 44 | 44 | 20 | 45 |

## Sample V

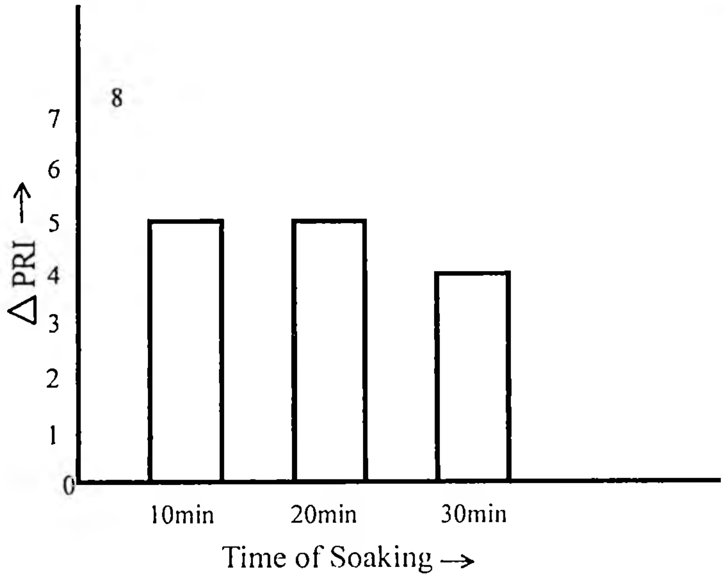
| | 10 min | | | 20 min | | | 30 min | | |
|---|---|---|---|---|---|---|---|---|---|
| | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI |
| Control | 55 | 29 | 53 | 55 | 29 | 53 | 55 | 29 | 53 |
| 0.1% oxalic acid | 54 | 31 | 57 | 51 | 29 | 57 | 52 | 29 | 56 |

## Sample VI

| | 10 min | | | 20 min | | | 30 min | | |
|---|---|---|---|---|---|---|---|---|---|
| | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI | $P_0$ | $P_{30}$ | PRI |
| Control | 53 | 26 | 49 | 53 | 26 | 49 | 53 | 26 | 49 |
| 0.1% oxalic acid | 51 | 27 | 53 | 50 | 27 | 54 | 52 | 28 | 54 |

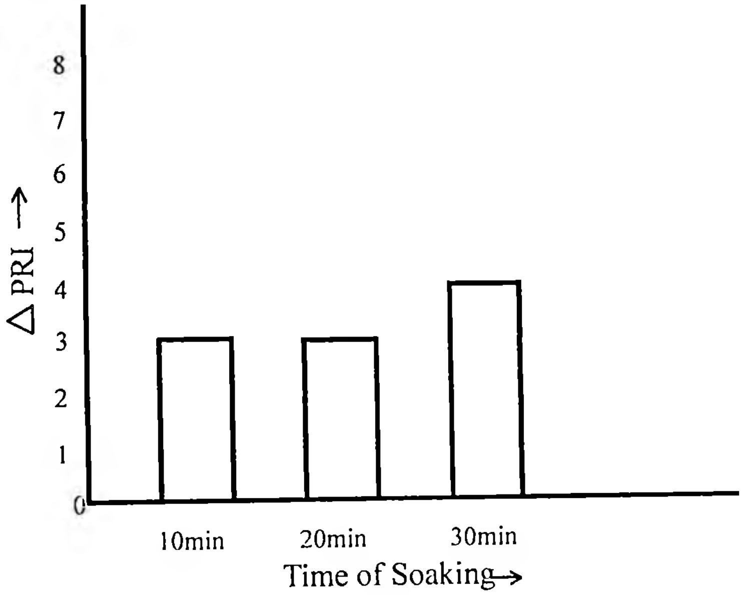
## Sample I

| Period of Soaking | 10 minute | 20 minute | 30 minute |
|---|---|---|---|
| Δ PRI | +5 | +5 | +4 |



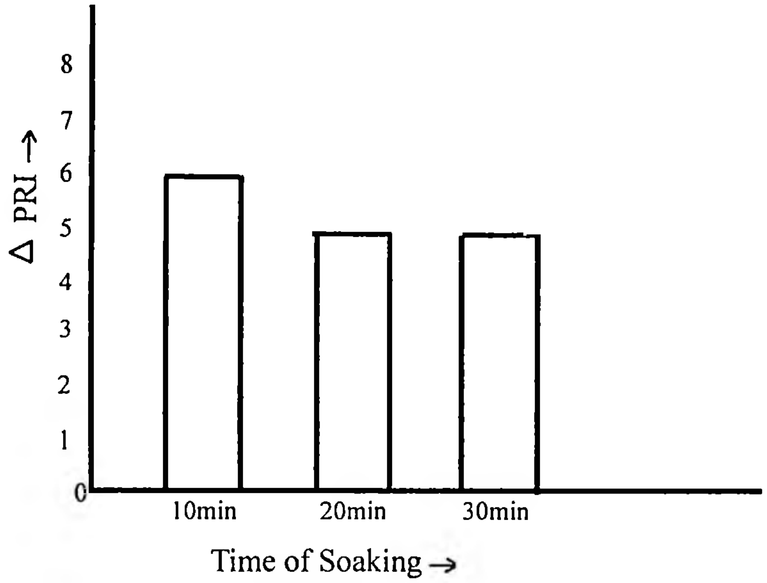
## Sample II

| Period of Soaking | 10 minute | 20 minute | 30 minute |
|---|---|---|---|
| Δ PRI | +3 | +3 | +4 |



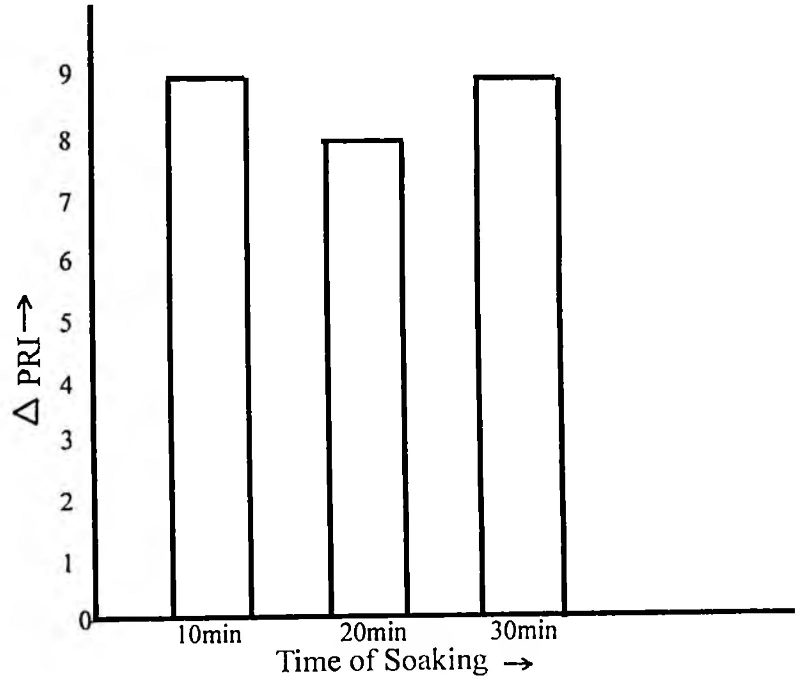
## Sample III

| Period of Soaking | 10 minute | 20 minute | 30 minute |
|---|---|---|---|
| Δ PRI | +6 | +5 | +5 |



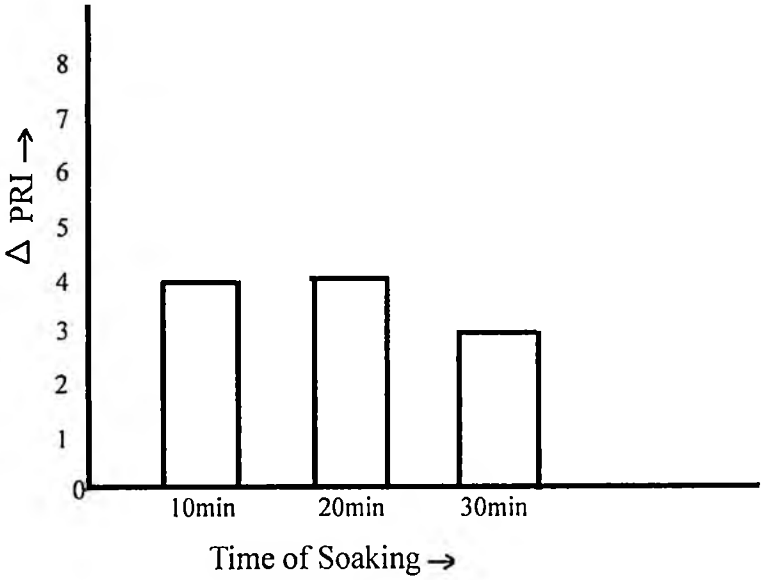
## Sample IV

| Period of Soaking | 10 minute | 20 minute | 30 minute |
|---|---|---|---|
| Δ PRI | +9 | +8 | +9 |



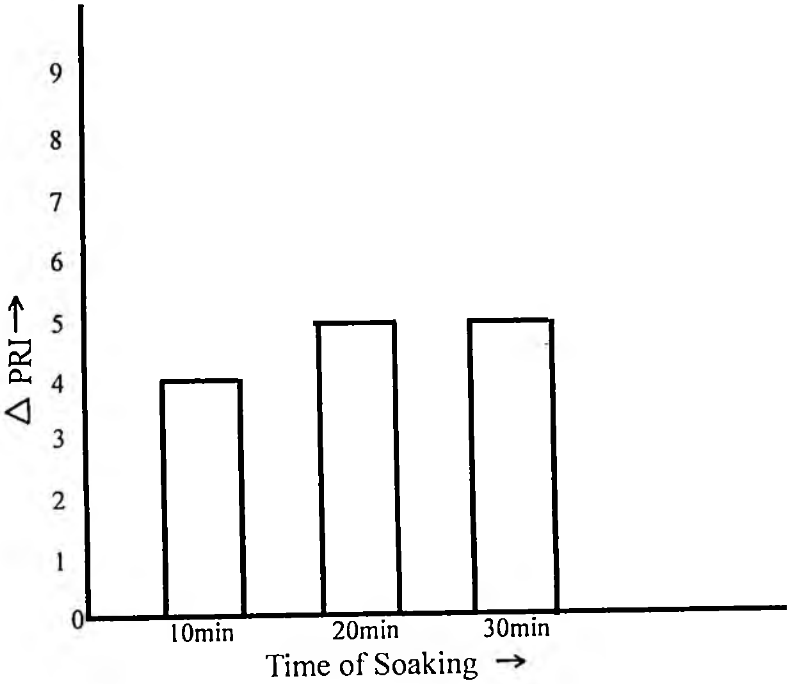
## Sample V

| Period of Soaking | 10 minute | 20 minute | 30 minute |
|---|---|---|---|
| Δ PRI | +4 | +4 | +3 |



## Sample VI

| Period of Soaking | 10 minute | 20 minute | 30 minute |
|---|---|---|---|
| Δ PRI | +4 | +5 | +5 |

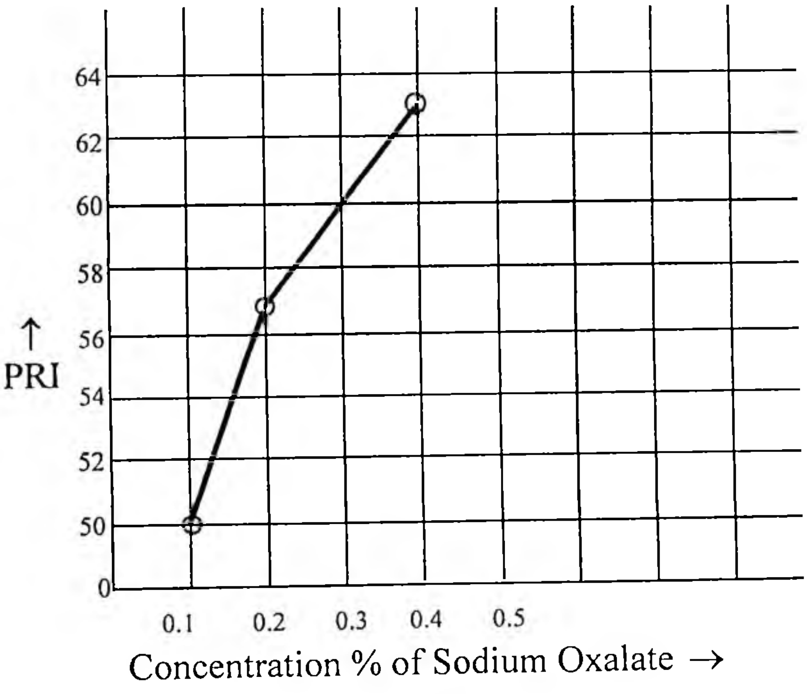


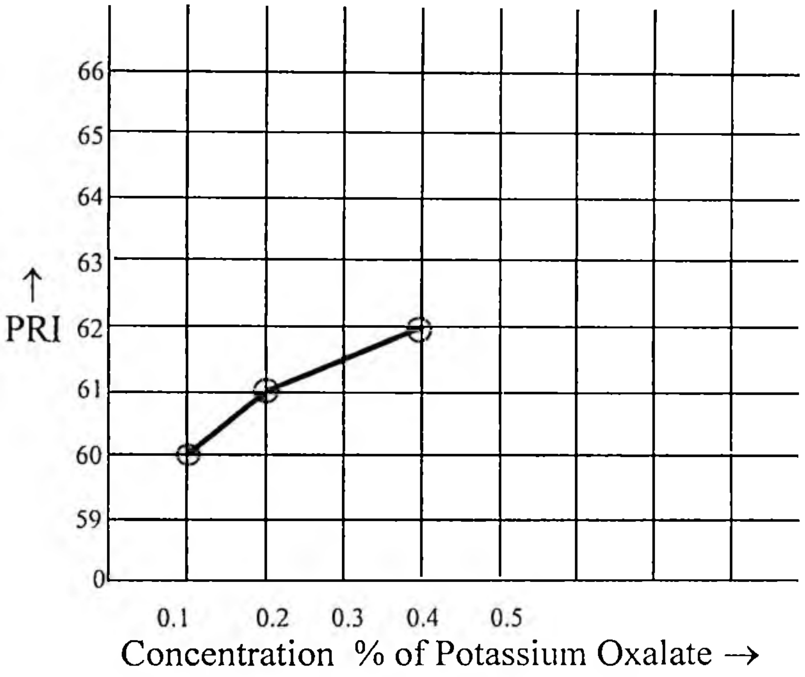
when crumbs of raw natural rubber are soaked in a solution of oxalic acid, for imparting protection to rubber oxalic acid has to enter into rubber. Entry of oxalic acid is via a diffusion mechanism since this a time controlled process, the optimum duration of soaking had to be decided. For this crumbs were soaked in 0.1% oxalic acid solution for varying duration and PRI of rubber were determined. The results obtained are shown in figure.

There is a marked increase in PRI on soaking the sample for 10 minute in oxalic acid. However when the duration of soaking is increased to 20 minutes and then to 30 minutes there is no marked increase in PRI over that achieved in 10 minute soaking.

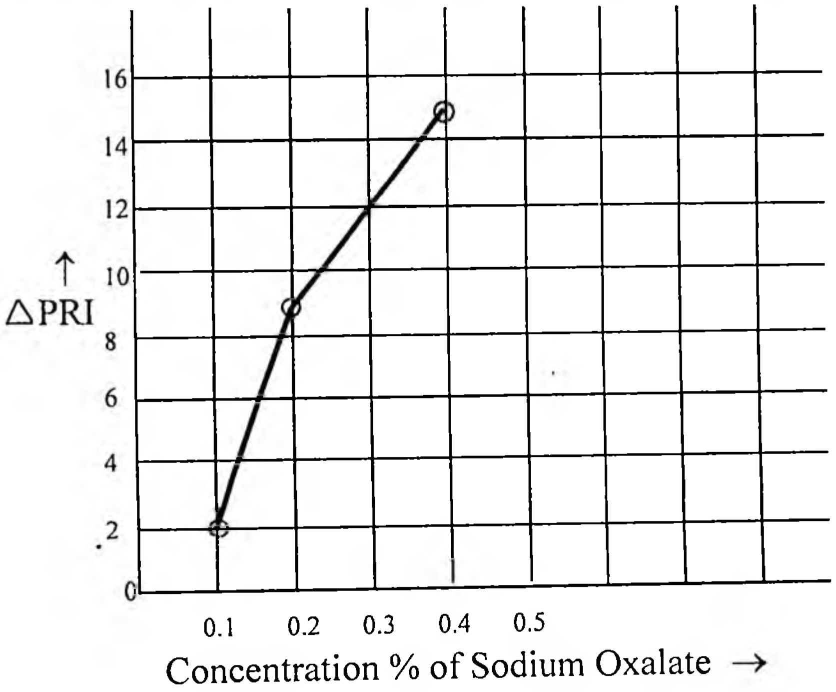
## 4.3 Effect of Addition of Oxalic Acid in Various Chemical Forms

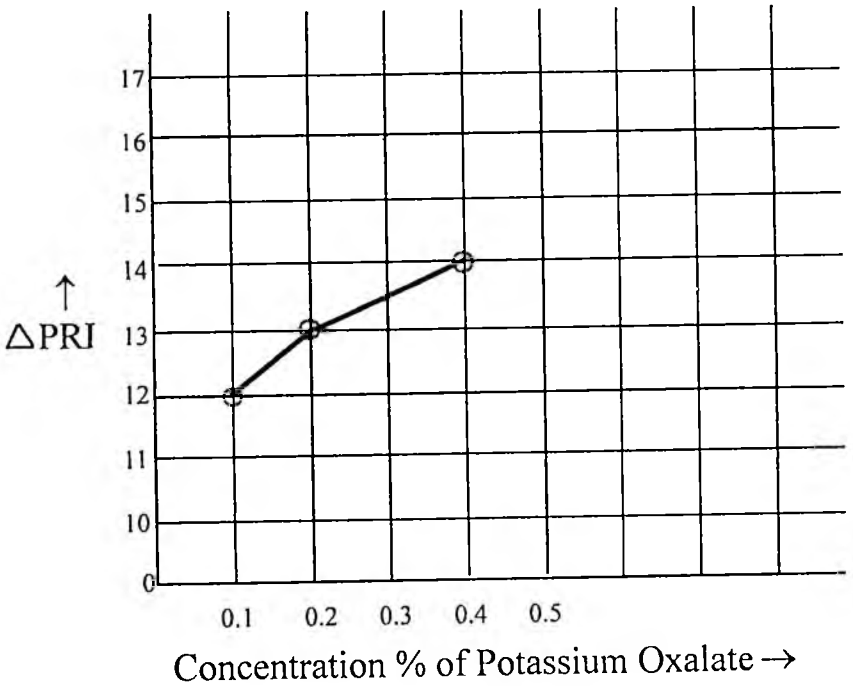
| Additive | 0.1% | | 0.2% | | 0.4% | |
|---|---|---|---|---|---|---|
| | $P_0$ | PRI | $P_0$ | PRI | $P_0$ | PRI |
| Control | 58 | 48 | 58 | 48 | 58 | 48 |
| Sodium Oxalate | 62 | 50 | 58 | 57 | 54 | 63 |
| Potassium Oxalate | 57 | 60 | 57 | 61 | 63 | 62 |





| Additive | 0.1% | 0.2% | 0.4% |
|---|---|---|---|
| | Δ PRI | Δ PRI | Δ PRI |
| Sodium Oxalate | +2 | +9 | +15 |
| Potassium Oxalate | +12 | +13 | +14 |





Oxalic acid, being acidic in nature, if retained in rubber after drying is likely to affect the rate of cure of rubber during product manufacture. If oxalic acid is added to rubber as water soluble salts, the acidity problems would be avoided. Hence trails were conducted by treating raw rubber with solution of sodium and potassium oxalates. The results obtained are shown in figure. It is observed that like oxalic acid, sodium oxalate and potassium oxalate are useful in improving the PRI of raw rubber. It is observed that reactivity is in the order.

**Potassium Oxalate > Sodium Oxalate > Oxalic Acid**

# CHAPTER V

# CONCLUSION

**Following conclusions are derived from this study**

- Soaking of wet crumbs in oxalic acid can improve the PRI of raw natural rubber
- Optimum concentration is found to be 0.1%
- Optimum duration of soaking was 10 minutes
- Reactivity of oxalate is in the order,

**Potassium Oxalate > Sodium Oxalate > Oxalic Acid**

••••••••••••••••••••••••••••

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