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TEST METHODS FOR RUBBER BLEACHING AGENTS

By

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The crepe rubber industry is an integral sector of the rubber industry in Sri Lanka and has gained the reputation of being the world's largest crepe rubber producer. Pale crepe is the purest grade of Natural Rubber produced in the world today. Apart from the high purity it has a very light, water white appearence and it's main use is in the production of light coloured non black rubber products. The best quality crepe rubber can be produced with Sri Lankan rubber latex due to it's inherent good qualities. However in the recent past, there have been a large number of quality claims for the crepe rubber exported from Sri Lanka thereby losing a substantial amount of foreign exchange to the country. This resulted from the discolouration of crepe rubber exported from Sri Lanka at the consumer's end. This discolouration occurs due to a number of reasons.

In the production of pale crepe from natural latex the clarity of the final product is achieved mainly by fractionation and/or bleaching. Some chemicals are employed to reduce the storage discolouration by inhibiting the enzymatic reactions occuring during storage of rubber. Bleaching agents are used to decolourise the naturally occuring pigments present in latex which are mostly of caratenoid type. The common bleaching agents employed for this purpose have been aromatic mercaptans. Xylyl mercaptan marketed as RPA–3 had been used as the only bleaching agent until the production of this chemical was banned in the USA due to it's high level of toxicity and the stock of RPA–3 produced was estimated to run out by 1979. This left the RRISL scientists to find a suitable alternative in a very short time to avoid the collapse of the Sri Lankan crepe rubber industry. The RRI scientists accepted this challange and their effort was successful in yielding a substitute for RPA–3 which also was a mercaptan called Tolyl Mercaptan and named as RRI–7. Subsequent experiments led to finding of a new water soluble bleaching agent which was a modification of the oil based Tolyl mercaptan

Both these oil based and water soluble bleaching agents are currently available in the market and used in the crepe rubber industry in Sri Lanka. Oil based bleaching agent is marketed as a 35% solution in petroleum solvent and the water soluble bleaching agent is marketed as a 35– 40% aqueous solution under different trade names.

In case the concentration of the bleaching agent is doubtful, checking the concentration of the chemical is of vital importance to the crepe rubber manufacturer enabling the incorperation of the correct amount of active ingredient to the latex to obtain crepe rubber with better colour. If excess is added rubber tends to soften especially when exposed to sunlight or heat. The active ingredient should be added at 35–50g on 100kg of dry rubber, decided upon by the amount of pigments present in latex which is a clonal characteristic and also is determined by the amount of fraction removed from latex. The addition of lower quantities than the recommended dosage will produce crepe rubber which may go into the lower grades. Therefore the strength or the active ingredient content of these bleaching agents should be determined if the user has any doubt regarding the purity of the chemical.

Methods of testing for oil based bleaching agents :

Two methods of testing the oil based bleaching agent are discussed here. One method is a titration method and the other is based on the crystallization behaviour of mercaptans in the solution of bleaching agent.

(A) Titration method:

In this method, an accurately weighed sample containing 1–2 milli equivalents of the mercaptan is dissolved in benzene, naphtha, octane or heptane (100 ml.). An exact portion of 10 ml. of this solution is transferred to a 250 ml Erlenmeyer flask followed by anhydrous methanol (100 ml). 0.005 N Silver nitrate solution (approximately 45 ml) is added from a burrette to this solution while swirling the flask vigorously. Ferric alum indicator (2 ml) is then added and the solution is titrated with 0.005N ammonium thiocynate solution until a faint pink end–point is reached. The pink colour is discharged by adding std. Silver nitrate in slight excess and the pink end–point is restored by titrating again with the std. thiocynate solution. Continuous agitation during the titration is extremely important.

Calculation : Calculate the mercaptan content of the sample stoichiometrically using the following equations.

$$RSH + Ag \longrightarrow RSAg + H^+$$
$$Ag^+ + CNS^- \longrightarrow AgCNS$$

However, our experience shows that the samples tested using the method described above, give highly errorneous results; the reason

for which is the oxidation of the mercaptan to disulphides on exposure to light. Therefore, this method is not suitable for the determination of mercaptan content of the oil based bleaching agent.

(B) Determination of the Saturation Temperature of the Tolyl Mercaptan Solution:

A very simple and easy method has been developed by the RRI to determine the active ingredient content of the oil based bleaching agent. The crystallisation behaviour of the bleaching agent is utilised in this method. It has been found that the crystallising temperature depends on the concentration of the active ingredient in the oil based tolyl mercaptan solution.

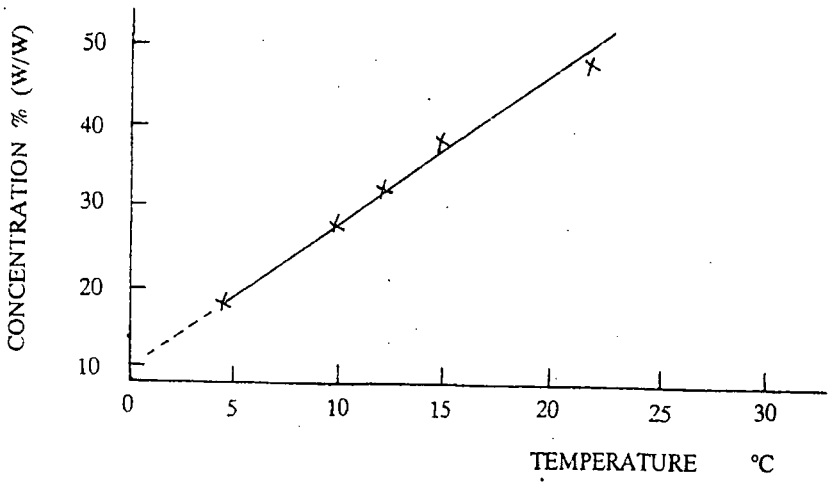
A calibration graph has been prepared by determining the crystallisation temperature of a series of tolyl mercaptan solutions of known strength. (Table 1).

Table 1

Percentage of active ingredient	Crystallisation temperature (°C)
50	22
40	15
35	12
30	10
20	5

Procedure:

A sample of the tolyl mercaptan solution to be tested is slowly cooled in a test tube while observing the temperature, by means of a thermometer inserted into the sample solution. The temperature is recorded at the first sign of crystal formation. Then the temperature is slowly raised and it is recorded as the last traces of crystals disappear. The mean value of these two readings is taken as the crystallisation temperature. Hence, the concentration of the tolyl mercaptan solution can be read from the calibration graph. (figure 1).



None of the above test procedures are applicable for the determination of the active ingredient content of the water soluble bleaching agent. The test method described below, which has been developed by the Raw Rubber & Chemical Analysis Department of RRI for the determination of the active ingredient content of the water soluble bleaching agent, is found to be a highly accurate analytical test method.

Determination of the sodium p. toluene thio phenate content of water soluble bleaching agent:

Reagents : Silver nitrate solution – standard 0.005N. Ammonium thiocyanate solution – 0.005N, standardised against the std. silver nitrate solution. Ferric alum indicator – Approximately 40g of ferric alum is dissolved in 100 ml of 1N nitric acid. The solution is boiled to remove nitrogen oxides, cooled and diluted with three volumes of distilled water.

Procedure:

0.6 – 0.7 g of the bleaching agent solution is weighed out accurately from a weighing bottle into a 250 ml volumetric flask and distilled water is added upto the mark. 25 ml of this solution are transfered to a 250 ml Erlenmeyer flask. 40 ml of 0.005N silver nitrate solution are added from a burette to the sample solution while swirling the flask vigourously,

followed by 2 ml of ferric alum indicator. The solution is then titrated against 0.005N ammonium thiocyanate solution until a faint pink end-point is reached.

Calculation:

$$\text{Active ingredient content of sodium p. toluene thiophenate solution} = \frac{146\ (40N'-N''V)}{W}\ \%\ (w/w)$$

where, N' = Normality of silver nitrate solution = 0.005
N'' = Normality of ammonium thiocyanate solution
V = volume of thiocyanate required for the titration(ml)
W = weight of the sample (g)

Laboratory Investigation :

A sample of the sodium para toluene thiophenate solution was prepared in the laboratory to investigate the applicability of the above titration method. The following quantities of ingredients were used to prepare this solution.

Tolyl mercaptan	—	62.3 g
Water	—	80.0 g
Sodium hydroxide	—	25.0 g
Total weight	—	167.3 g

Assuming, the thiol is completely converted to the sodium salt, the weight of the sodium salt being formed = 73.35g

Therefore, the expected concentration of the salt solution

$$= \frac{73.35}{167.3} \times 100$$
$$= 43.84\%\ (w/w)$$

The concentration of this solution, when determined using the titration method described above, was found to be 44.095% (w/w) which was agreeable with the expected value.

Discussion:

In this titration, a known volume of std. silver nitrate solution is added in excess, when it reacts with the sodium salt of tolyl mercaptan

to form a precipitate which is greyish yellow or light yellow in colour. The excess of silver nitrate added is then titrated with std. ammonium thiocyanate solution. Based on these readings, the equivalents of the salt reacted with silver nitrate can be calculated using the following equations.

$$CH_3.C_6H_6.S^-Na^+ + Ag^+ \longrightarrow CH_3.C_6H_6.SAg + Na^+$$

$$Ag^+ + CNS^- \longrightarrow AgCNS$$

Therefore, the strength of the initial mercaptan solution can be worked out. The calculation formulated in this method is for the sodium salt of tolyl mercaptan. This formula may be adjusted where necessary in the case of other water soluble bleaching agents.

The interference of the colour of the silver precipitate sometimes makes it difficult to detect the pink end-point. Therefore it is advisable to discharge the colour of the end point with excess silver nitrate and restore it again with the std. thiocyanate solution.

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REFERENCES

Annl. Revw. of the Rubb. Res. Inst. of Sri Lanka. (1982.) 105–109

Tillekeratne, L. M. K., Sarath Kumara, P. H., Weeraman, S., Mahanama, M., Nandadeva, R. (1984). A study of the mechanism of action of alkaline metal salts of aromatic thiols on carotenoid compounds Present in NR latex. **Proc. Int, Rubb. Conf.** 1984, Colombo. **2(1)** 89–95.

Welcher, F. J. (1963). Std. Methods of Chemical Analysis, 6th ed, vol. 2, pp. 500, New York; D.Van Nostrand Company, Inc..