STUDIES ON ARSENICAL CREOSOTE AS A WOOD PRESERVATIVE FOR MARINE STRUCTURES

PART I INCORPORATION OF ARSENIC IN CREOSOTE AT VARIOUS TEMPERATURES

N. UNNIKRISHNAN NAIR, A. G. GOPALAKRISHNA PILLAI AND R. BALASUBRAMANYAN
Central Institute of Fisheries Technology, Craft and Gear Division, Cochin-11.

A detailed study of the fortification of normal creosote and low temperature creosote with As_2O_3 at 40°C, 50°C, 60°C, 70°C, 80°C & 90°C was carried out. When compared to normal creosote, low temperature creosote has been found to combine more easily with As_2O_3 when temperature was raised from 40 to 90°C. The incorporated arsenic values obtained shows that low temperature creosote with high phenolic content, retains considerably more As_2O_3 and a maximum of 0.2180% w/w can be incorporated in low temperature creosote at 90°C.

INTRODUCTION

Although wood preservatives and wood preservation techniques have shown enormous strides, no one sure method has yet been found and standardised for the prevention of marine wood boring organisms attacking timber structures exposed to sea water. This problem continues to remain unsolved in the tropical waters of India, where innumerable wooden fishing crafts and boats are still resorting to costlier methods of protection in the absence of any cheaper and effective alternatives. Coal tar distillates and derivatives have been in use for wood preservation throughout the world well over a century. Creosote oils impart fire resistance to the treated poles (Keating 1962), retard splitting and give excellent results against decay under terrestrial conditions. Narayanamurthi (1942, 1951), Pande (1955), Purushotham *et al* (1961, 1962), Pande and Jain (1967), Pande *et al* (1967), and Jain *et al* (1968) did pioneering work on creosote in India. Creosote as such has been found to be somewhat effective against some of the marine wood boring organisms only at different levels of loading ranging from 8 kg/m^3 to a maximum of 320 to 352 kg/m^3 (Balasubramanyan 1964 and Balasubramanyan *et al* unpublished records). Johanson (1969a) is of the opinion that wood treated with creosote becomes unpalatable to termites. Following the termiticide investigations carried out at the laboratories of the Commonwealth Scientific and Industrial Research Organisation of Australia where further fortification of wood preservatives with certain toxic chemicals has enhanced the preservative effect and reduced the loading, the Central Institute of Fisheries Technology at Cochin took up investigations on the fortification of creosote with arsenic trioxide and the resultant mixure was utilised as a preservative on timber test blocks of Mango *(Mangifera indica)* and Haldu *(Adina cordifolia)* as a protection against common wood borers. These timber species have been selected for studies due to their suitability for boat-building, their cheapness in price and easy availability besides their amenability to quick seasoning and preservative treatment. The present paper attempts to describe the characteristic dissolution of arsenic in creosote under varying temperatures which seems to be an important prerequisite for an enhanced preservative effect.

MATERIAL AND METHODS

Normal creosote from a commercial source and the low temperature creosote produced by the Regional Research Laboratory, Hyderabad (CSIR) were examined for their affinity towards arsenic trioxide. The preparation procedure is the same as that followed by Johanson (1967). It consisted of heating known quantities of As_2O_3 with known quantities of low temperatue creosote and normal creosote in 250 ml stoppered conical flasks for five minutes at 90°C over a water bath. The mixtures thus obtained were allowed to stand to settle out during the next 24 hours at 40°C, 50°C, 60°C, 70°C, 80°C and 90°C as required. At the end of the settling periods and while maintaining their temperatures, the preparations were filtered through Whatman No. 42 filter paper. The stock samples of arsenical creosotes thus prepared were kept separately for subsequent tests.

TABLE I DISTILLATION DATA OF THE TWO CREOSOTES TESTED

Preparation	Specific gravity at 30°C	Moisture % by volume	Benzol insoluble %	Coke residue % by wt.	Tar acids V/W %	Flash point	Distilltion fraction % (ISI method)	Residue above 355°C
RRL creosote * (low temperature creosote)	0.9693	0.5	0.0328	2.1488	22	140	Upto 210°C 2.87 ,, 235°C 13.14 ,, 315°C 46.66 ,, 355°C 19.78	15.61
** Normal creosote	1.0576	1.5	0.0452	3.2095	5.0	176	Upto 210°C 9.12 ,, 235°C 22.38 ,, 315°C 35.82 355°C 21.7	10.12

* Reproduced from Jain *et al* (1968)

** Reproduced from Pande, *et al* (1967)

ANALYTICAL METHOD

The procedure employed for determining the arsenic dissolved in creosote was also the same as that followed by Johanson *(loc cit)*. The reagents employed were all of analytical grade purity. Weighed to the nearest mg between 0.5 to 1.0 g from the stock arsenical creosote prepared earlier, into 250 ml conical flask. Added one glass ball, 20 ml conc. H_2SO_4 and swirled to mix. Then commenced adding 100 volume hydrogen peroxide dropwise and controlled the reaction by the rate of addition of hydrogen peroxide. When the reaction slowed down, the digest was heated and the temperature of the digest was adjusted just high enough to produce white fumes. The discrete addition of hydrogen peroxide was continued until the digest cleared. At the end of digestion care was taken to keep at least 20 ml of H_2SO_4 present. The digest was cooled, added 10 ml of distilled water and 220mg hydrazine sulphate, boiled until a ring of sulphuric acid condensed 1/16 inch from the top of the lip of the conical flask. At this stage all the excess of hydrazine sulphate was expelled. Then the digest was cooled, diluted with 100 ml water, added 10 ml HCl and 2 drops of methyl orange indicator and titrated against 0.005N $KBrO_3$ until just colourless. Obtained a titration blank by digesting reagents only and the blank correction determined.

1 ml 0.005N $KBrO_3$ = 0.2473 mg As_2O_3 = 0.1873 mg arsenic. In practice, the relationship 4.04 ml of 0.005 N $KBrO_3$ = 1 mg As_2O_3 can be used. Arsenic trioxide was reported as percent w/w in creosote.

TAELE II PERCENTAGE ARSENIC TRIOXIDE TAKEN UP BY THE TWO CREOSOTES AT VARIOUS TEMPERATURES W/W.

	Low temperature creosote		Normal creosote	
Temperature °C	%As_2O_3 combining	% rate of increase	%As_2O_3 combining	% rate of increase
40	0.01522		0.00300	
50	0.16176	962.8	0.01230	310.0
60	0.14260	-11.8	0.02623	113.3
70	0.15220	5.6	0.03327	26.8
80	0.19180	26.0	0.03779	13.6
90	0.21800	13.7	0.03840	1.6

RESULTS AND DISCUSSION

Earlier attempts (Hill 1921, Cummins *et al* 1930, Johanson 1965, 1966, 1967, 1969a 1969b, 1969c, 1969d and 1970) with fortified creosote have given encouraging results against terrestrial termites but no investigation appears to have been initiated for its efficacy against marine wood boring organisms. Fortification of creosote with arsenic not only makes it more toxic, but also prolongs the efficiency of preservative effect on treated timbers. The reaction products get very well fixed into wood thus preventing leaching of the preservative. For health and enconomic reasons arsenic has an advantage over chlorinated hydrocarbon groups (Johanson 1965). Arsenical creosote is not corrosive and it only tends to inhibit corrosion as has been reported by Syers *et al* (1966) and Johanson *et al* (1968).

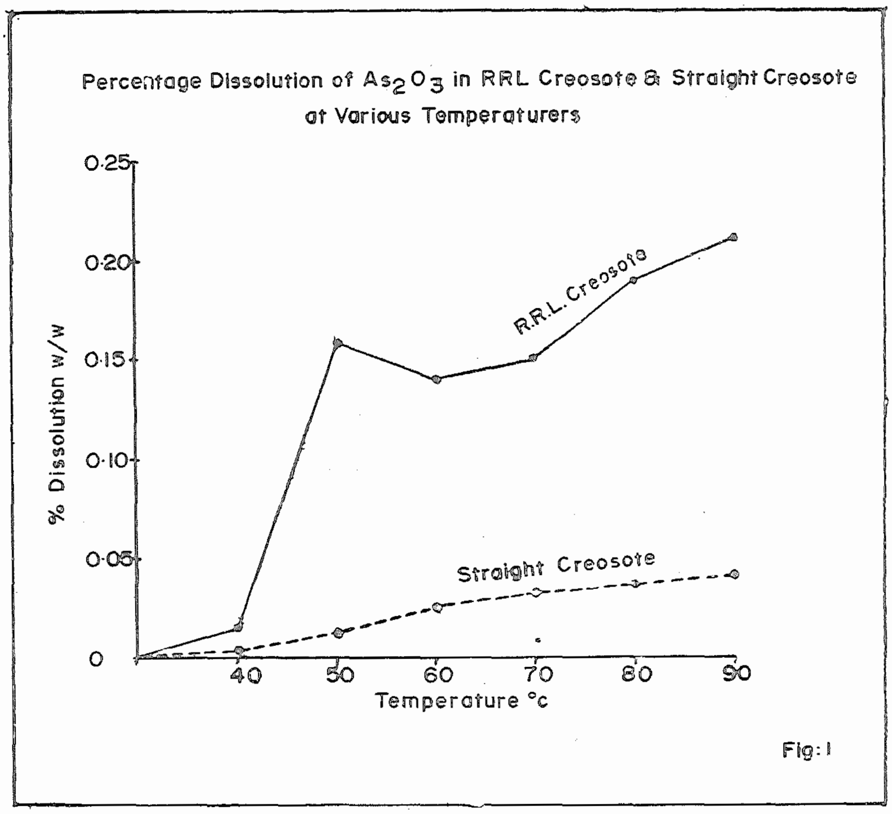

Fig: I

The data presented in Table 1 and Fig 1 indicate that the low temperature creosote produced by the Regional Research Laboratory has the largest capacity for arsenic trioxide when compared to the normal creosote. A maximum of 0.218% w/w was absorbed by RRL creosote at 90°C while the normal creosote absorbed only 0.0384% w/w at equivalent temperature. As evident from Table II, an increase from 0.003 to 0.03840 (10 times) % w/w absorption was noticed in normal creosote, while an increase of 0.01522 to 0.2180% w/w (20 times) was noticed in RRL creosote, evidently establishing its greater affinity for arsenic. In both cases the percentage of increase was more when the temperature was raised from 40 to 50°C compared to other temperatures. Johanson (1966) found that the phenolic content of creosote influences its affinity for As_2O_3. He has tested creosote with 3.0, 4.5, 5.6, 18.8 and 23.7 % v/w phenols and incorporated 0.02, 0.07, 0.08, 0.26 and 0.41 % w/w As_2O_3 respectively. Table 1 shows higher phenolic content (tar acids) in low temperature creosote. The incorporated arsenic values (Table II) obtained in this study show that low temperature creosote with a high phenolic content, retains considerably more As_2O_3 than normal creosote. It is apparent, therefore, that low temperature creosote with high phenolic content is thus suitable for arsenic fortification.

Comparison of the data obtained in this investigation with those of Australian creosote and wood tar oil preparations (Johanson 1965) shows higher absorption of arsenic by Australian preparations. Johanson (loc cit) recorded 0.2% w/w to 0.36% w/w concentration of arsenic trioxide in Australian creosote at 40°C. He observed that values increased in brown coal tar creosote and victorian creosote when temrature increased from 40 to 60°C. The values increased from 0.36% and 0.21% to 0.59% and 0.3% for the two types of creosotes respectively. In the present investigation, elevation of settling temperature produced higher absorption in low temperature crosote, compared to straight creosote. Pande and Jain (1967) found the low temperature coal-tar creosote equally satisfatory as a substitute for normal creosote. Low temperature creosote has the advantage of low price and higher affinity for arsenic thus making it more suitable for all marine exploitations.

ACKNOWLEDGEMENT

The authors are thankful to Dr. V. K. Pillai, Director, Central Institute of Fisheries Technology and Shri G. K. Kuriyan, Head of Divison (Craft & Gear) for all encouragements. We are indebted to Dr. R. Johanson, Forest products Laboratory, Melbourne, Australia, for readily providing us with literature on arsenical creosote and also for suggesting the detailed procedure for the estimation of arsenic in creosote. Sincere thanks are also due to the Director, Regional Research Laboratory (CSIR), Hyderabad, for the free sample of low temperature creosote for our experimental studies.

REFERENCES

Balasubramanyan, R. 1964. *Proceedings of the Symposium on Marine Paints,* N. C. M. L. Bombay, Nov. 20/21, 120-123.

*Cummins, J. E., Dadswell, H. E., and Hill, G. F. 1930. *J. Counc. Sci. Ind. Res., (Aust),* **3**, 133-148.

Jain, J. K., Pande, J. N., Sharma, R. P., and Purushotham, A. 1968. *J. Timb. Dry. Preserv. Ass India,* **XIV** (**4**), 6-24.

Johanson, R. 1965. *J. Inst. Wood Sci.,* **3** (**15**), 36-44.

———, 1966. *Chem. and Ind.,* **29**, 1269-1270.

———, 1967. *J. Inst. Wood Sci.,* **4** (**19**), 15-26.

———, 1969a. *Australian Power Engineering,* **9** (**5**).

———, 1969b. *J. Appl. Chem.,* **19**, 201-204.

———, 1969c. *Ibid, 205-208*

———, 1969d. *Holzforschung,* **23** (**6**), 181-184.

———, 1970. *Ibid,* **24** (4), 137-141

——— & Syers, T. 1968. *CSIRO, Division of Forest Products, Project 9-17. Laboratory report No. 2.*

Keating, W. G. 1962. *CSIRO Forest Products News Letter* No. 286.

*Narayanamurthi, D. 1951. *Indian Forest Bull* No. 144.

*Narayanamurthi, D & Ranganathan V. 1942. *Ibid,* No 104 New series.

Pande, J. N. 1955. *J. Timb. Dry. Preserv. Ass. India.,* **2** (**1**).

Pande J. N. & Jain, J. K. 1967. *Ibid,* **XIII** (**2**), 9-15.

Pande, J. N., Sharma, R. P., & Jain J. K. 1967. *Ibid,* **XIII** (**3**), 3-5.

Purushotham, A. 1964. *Ibid,* **X** (4), 9-11.

Purushotham, A., Pande, J. N., Mukerji, H. K. & Chandola, L. P. 1961. *Ibid,* **VII** (**1**), 2-19.

Purushotham, A., Pande, J. N., Mukerji, H. K. & Chandola, L. P. 1962. *Ibid,* **VIII** (**3**), 11-29.

---

* Not consulted in original.