PRESERVATION OF COTTON FISH NET TWINES BY TANNING II. FIXATION OF TANNIN.

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Fixative behaviour of tannin belonging to three functional groups was studied in detail using copper sulphate and potassium dichromate as oxidising agents.

Tanning materials belonging to three functional groups such as pyrogallol, catechol and mixed were selected and their relative fixative behaviour using copper sulphate and potassium dichromate was studied in detail.

Kuriyan and Nayar (1961) state that the preservatives used by local fishermen of India are of indegenous origin and that the method of protection of fishing gear is to give a coating of tannin. Cecily and Kunjappan (1971) analysed the tannin content of the different raw materials and categorised them as pyrogallol, catechol and mixed tannins and evaluated the optimum concentration of tannin in dye bath to get the maximum effectiveness. Since tannin is watersoluble, intermittant or prolonged exposure of nets in water leaches the tannin which in consequence reduces the preserving power. The fishermen make up this tannin loss by frequent retreatments of their nets at intervals ranging from once a fortnight to once a month (Clague and Datingaling 1950, Sulit and Panganiban 1954, Takayama and Shimozaki 1957, Miyamoto and Shariff 1959 and Kuriyan and Nayar loc. cit).

Solubility of tannin in water can be considerably minimised by oxidation. Anon (1952) and Miyamoto (1958) report repeated tanning and drying which allows oxidation of certain amount of tannin. For accelerating the process of oxidation of tannin, various chemicals are also used. Farar (1949) and Alkins and Warren (1953) mention the use of copper sulphate as oxidising agent, while Rix (1951), Clague and Datingaling (op. cit) Chubb (1954), Klust (1954), von Brandt (1955), Anon (1957) and Takayama and Shimozaki (1957) have used either copper sulphate or dichromate of sodium or potassium. The use of an admixture of copper sulphate and potassium dichromate was also reported by Zederler (1950), Anon (1956) and von Brandt (1957).

The present paper is an evaluation of the action of fixatives on the different tan-

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nin groups following various methods of applicaton.

Materials And Methods

One sample each from the three representative groups of tannin were selected for the present study. Table I gives detailed analysis of the raw materials. The preparation of tannin dyeing bath and the treatment were similar as stated by Cecily and Kunjappan (op. cit). Fixative reagents selected were copper sulphate and potassium dichromate. The methods of fixation were as follows:

Table I The particulars of tanning material

Material	Terminaliachebula (Kadukka)	Odina wodier (Kalasm)	Dispyrosembryopteris (Panachikka)
Type of Tannin	Pyrogallol	Catechol	Mixed
Total solubles	71.52	18.51	19.04
Tannin content	41.54	10.10	10.16
Non tannins	30.03	8.42	8.88
Insolubles	15.37	19.30	25.65
Moisture	12.55	61.58	55.81
pH	3.40	4.50	5.00

1. Intermittant tanning and fixation using copper sulphate:

The method is similar to Olie's method or Dutch method (Olie 1918), von Brandt 1955 (op. cit), Koura (1963) except that instead of 2% and 4% cutch, the tannin content in dye bath was kept constant at 1% for the initial and 2% for final treatment irrespective of the tannin group. Fixation treatments were carried out in ammonical copper sulphate solution (1%). In order to study the effect of concentration of tannin on fixation, a second set of twine was also prepared using 2% tannin for the initial and 4% for final treatment following similar methods of fixation.

2. Repeated tannin treatment and single fixation using copper sulphate: After the initial treatment in 1% tannin, the dried twines were redyed in 2% tannin and finally fixed. A second set of twines was treated in 2% and 4% tannin respectively with subsequent fixation by ammoniacal copper sulphate.

3. Intermittant tanning and fixation by potassium dichromate:

The method is similar to special tanning or special gerbung process described by von Brandt (op. cit) and Koura (op. cit). Here also the steps followed are similar as in (1) with the differnce that fixation was carried out in a warm (40°C) solution of 3% potassium dichromate.

4. Repeated tanning and single fixation using potassium dichromate:

The method is similar to (2) except that the fixative is potassium dichromate.

After the fixation treatments the

twines were thoroughly washed in water. Special care was taken in the case of fixation by potassium dichromate by washing the twines in running water for 18 hrs. to free the material from crystallistation of excess chromates within the fibres which otherwise cause severe damage to the net.

The impregnation of the treatments following various methods of fixation was determined on the basis of the difference in weight of the material before and after treatments. The data collected are presented in Table II.

TABLE II THE IMMERSION PERIOD AND THE HYDROGRAPHIC CONDITION OF THE TEST SITE

Period of exposure : 4.9. '67 to 11.12. '67						
	Surface temperature (°C)			Salinty (‰)		
Period	Av.	Min.	Max.	Av.	Min.	Max.
Sept. 1967	27.8	26.0	29.0	13.45	1.6	20.4
Oct. 1967	29.6	28.5	31.0	13.40	8.9	24.9
Nov. 1967	29.0	28.0	30.5	22.10	14.7	33.1
Dec. 1967	29.1	28.5	30.0	31.90	28.1	34.0

The twines were then subjected to continuous immersion tests in the Cochin backwaters. The data on water-temperature and salinity at the test site during the period of investigation are presented in Table III.

TABLE III THE PERCENTAGE IMPREGNATION

Tannin group	Concentration of tinnin bath	Percentage Impregnation				
		Unfixed	Fixed by Copper sulphate & Amonia		Potassium Dichromate	
			Intermittant tanning	Repeated tanning	Intermittant tanning	Repeated tanning.
Pyrogallol	1%	4.13	15.04	5.19	16.16	9.22
(Kadukka)	2%	6.41	22.62	6.96	21.45	13.39
Catechol	1%	3.97	11.41	5.14	13.79	6.60
(Kalasm)	2%	4.40	14.63	6.83	16.09	9.67
Mixed	1%	3.65	12.58	4.82	16.37	7.28
(Panachikka)	2%	4.94	17.41	4.15	11.12	8.26

The strength of twines was determined periodically.

Results

The course of rotting of unfixed and fixed twines by different methods along with control is presented in text figures 1-5 which show the retention of strengh with respect to number of days of continuous immersion.

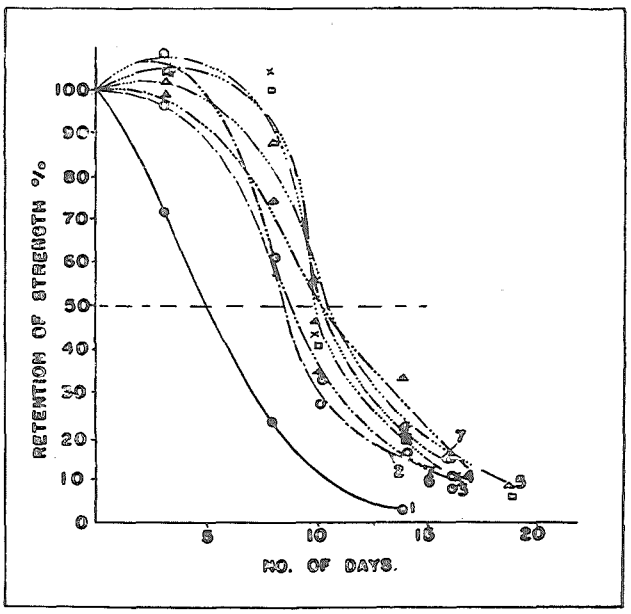

Fig. I Unfixed

1. Control
2. Pyrogallol
3. ,, ,, 2%
4. Catechol 1%
5. ,, ,, 2%
6. Mixed 1%
7. ,, ,, 2%

Discussion

Impregnation: The general trend of the take up of preservatives is more or less in a similar pattern among the three groups of tannin in the unfixed and fixed conditions. 1. Intermittant tanning and fixation using both copper sulphate and potassium dichromate register high values of impregnation.

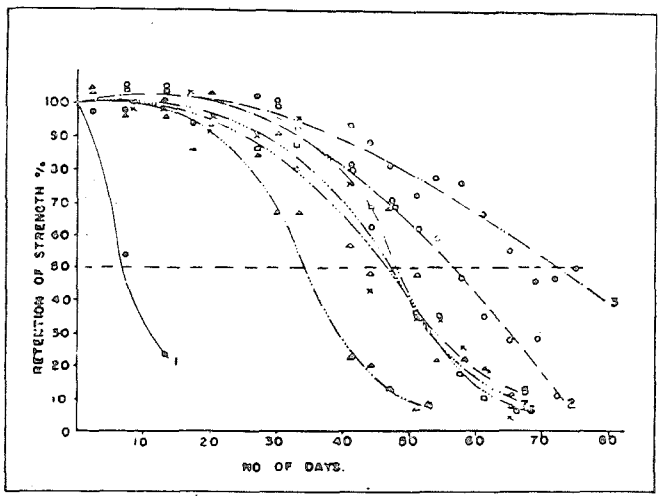

Fig. II Intermittant tanning and fixation by copper sulphate

1. Control 1%
2. Pyrogallol 2%
3. ,, ,, 2%
4. Catechol 1%
5. ,, ,, 2%
6. Mixed 1%
7. ,, ,. 2%

2 Among repeated tanning and single fixation those treated with copper sulphate gives comparatively lower weight values than potassium dichromate.

3. The impregnation values are found to be on the higher side with respect to concentration of tannin bath.

Effectiveness: The data on effectiveness were calculated from text figures 1-5 by method given by Nayar et. al. (1962) and are presented in Table IV.

It has been established earlier by many workers that fixation of tannin enhances the effectiveness of tannin preservaties. Alkins and Warren (loc. cit) found that preservation by cutching and fixation by copper sulphate enhanced the effectiveness nearly by two times. Farar (loc. cit) claims the superiority of copper sulphate while Koura (loc. cit) opines that when copper

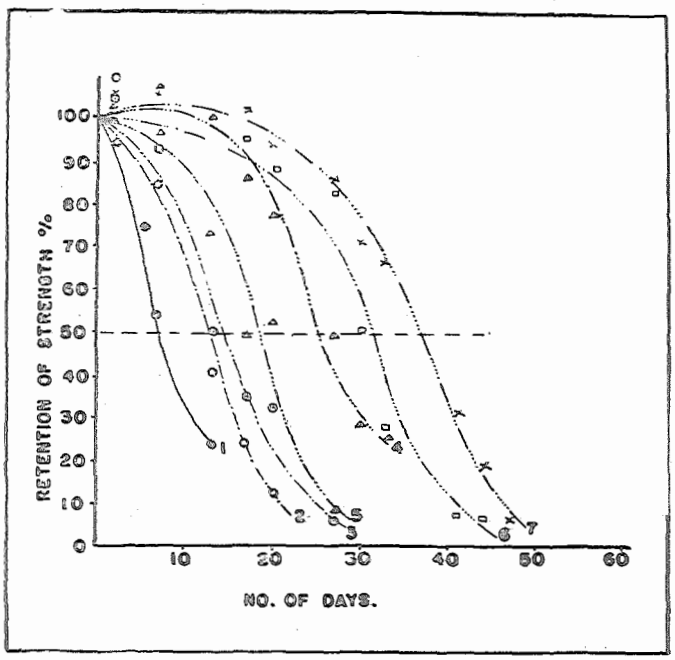

Fig. III Reported tanning and fixation using copper sulphate

1. Control
2. Pyrogallol 1%
3. ,, ,, 2%
4. Catehol 1%
5. ,, ,, 2%
6. Mixed 1%
7. ,, ,, 2%

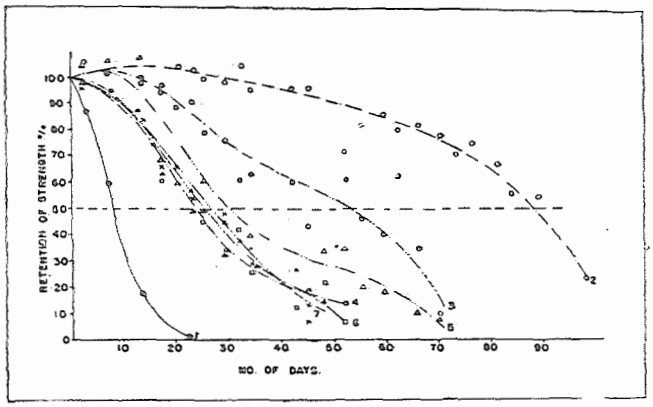

Fig. IV Intermittant tanning and fixation using potassium dichromate.

1. Control
2. Poyrogallol 1%
3. ,, ,, 2%
4. Catechol 1%
5. ,, ,, 5%
6. Mixed 1%
7. ,, ,, 2%

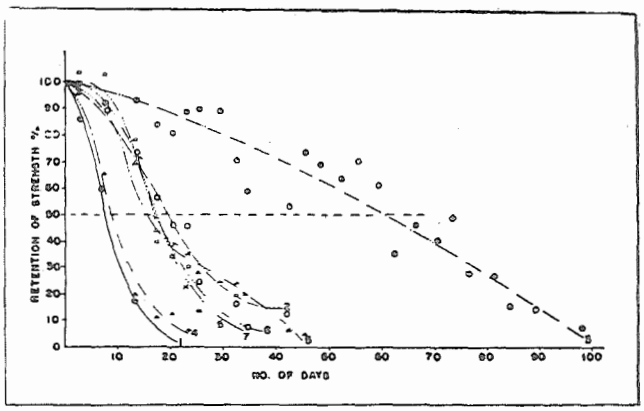

Fig. V Repeated tanning fixed by potassium dichromate

1. Control
2. Pyrogallol 1%
3. ,, ,, 2%
4. Catechol 1%
5. ,, ,, 2%
6. Mixed 1%
7. ,, ,, 2%

salts are used as fixative, in tropical area the high salinity acts as a limiting factor in the preservative effect as copper ions get exchanged with other metallic ions present in the sea water. Work done by Kuriyan and Nayar on cotton twines (loc. cit), Nayar and Naidu on manila (1962), Nayar *et. al.* on sisal (loc. cit), Nayar and Naidu on coir (1962) and George and Radhalekshmy (1962) on sun hemp twines showed that the effectiveness of various tannin preservatives fixed by copper sulphate and ammonia varied from 1.7 -3.99. Regarding fixation by potassium dichromate, Takayama and Shimozaki (loc. cit) have found that the application of dichromate could prolong the life of cutch treated twines twice. von Brandt (op. cit) on comparing Olie's method with special tanning method found the latter superior. Koura (loc. cit) and Radhalekshmy and Kuriyan (1969) while studying the temperature and salinity variations on the degree of rotting at temperature and tropical zones have also come to conclusion that

TABLE IV THE EFFECTIVENESS OF VARIOUS TREATMENTS

Tannin group	Concentration of tannin bath	Effectiveness				
		Unfixed	Fixed by Copper sulphate & Amonia		Potassium Dichromate	
			Intermittnat	Repeated	Intermittant	Repeated
Pyrogallol	1%	1.67	7.50	1.73	11.10	2.50
(Kadukka)	2%	1.72	9.60	1.93	6.60	7.50
Catechol	1%	2.00	4.53	3.40	2.96	1.13
(Kalasm)	2%	2.05	6.26	2.54	3.68	2.00
Mixed	1%	2.08	6.46	4.23	3.12	2.21
(Panachikka)	2%	2.06	6.32	4.96	3.38	2.21

potassium dichromate is more effective than copper sulphate at both places.

The data collected on the strength of twines at periodic intervals were statistically analysed. The breaking strength ($\bar{x}$), variance (s^2) and coefficient of variation (C.V %) were calculated and are presented in Table V.

TABLE V STATISTICAL ANALYSIS OF THE DATA

Type of tannin	Concentration of tannin.	*n	$\bar{x}$	s	C.V%
1. Unfixed					
	Control	5	45.34	39.78	87.74
Pyrogallol	1%	5	61.58	38.07	61.82
(Kadukka)	2%	5	46.68	40.58	86.93
Catechol	1%	5	70.18	31.33	44.64
(Kalasm)	2%	5	74.72	32.55	43.56
Mixed	1%	5	74.16	39.78	53.64
(Panachikka)	2%	5	75.24	39.29	52.22

* n = number of observations.

Contd.....

1	2	3	4	5	6
2. Intermittant tanning fixed by copper sulphate and amonia					
	Control	6	45.65	45.68	100.06
Pyrogallol	1%	6	101.61	3.07	3.01
	2%	6	98.11	2.96	3.02
Catechol	1%	6	100 50	4.06	4.04
	2%	6	96.70	5.74	5.93
Mixed	1%	6	99.53	3.66	3.68
	2%	6	98.91	3.77	3.82
3. Repeated tanning fixed by copper sulphate and Amonia					
	Control	6	45.65	45.68	100.6
Pyrogallol	1%	6	61.73	41.16	66.68
	2%	6	69.03	33.56	48.62
Catechol	1%	6	95.33	11.09	11.63
	2%	6	76.50	23.16	30.27
Mixed	1%	6	95.08	4.41	4.64
	2%	6	101.33	4.08	4.03
* n = number of observations.					
4. Intermittant tanning fixed by potassium dichromate					
	Control	10	26.84	40.80	152.01
Pyrogallol	1%	10	101.38	2 94	2.89
	2%	10	89.01	12.93	14.53
Catechol	1%	10	67.03	27.16	40.52
	2%	10	74.05	27.90	37.68
Mixed	1%	10	69.45	23.48	33.31
	2%	10	69.55	23.07	33.17
5. Repeated tanning fixed by Potassium dichromate					
	Control	10	26.84	40.80	152.01
Pyrogallol	1%	10	58.91	31.06	52.72
	2%	10	89.75	8.57	9.55
Catechol	1%	10	32.33	40.67	125.80
	2%	10	56.48	31.90	56.48
Mixed	1%	10	54.15	38.72	71 50
	2%	10	44.08	49.34	111.93

The average breaking strength is taken as a meaure of effctiveness and coefficient of variation as consistency. Higher thc value of coefficient of variation less is the consistency. Based on the statistical analysis and effectiveness data (Table IV) the following conclusions are derived.

1. In the unfixed state among the three groups of tannin catechol and mixed are found to be more effective than pyrogallol. This conforms to the findings made earlier by Cecily and Kunjappan (op. cit). But on fixation, pyrogallol tannin shows excellent preservative effect. It is very likely that this is due to greater solubility of pyrogallol tanning used for the experiments as evidenced by the high percentage of total solubles in it (Table I). Hence it is advisable to adopt fixation method when pyrogallol tannin is attempted for preservation of fishing gear.

2. Pyrogallol tannin shows very good results with both copper sulphate and potassium dichromate fixation except in repeated tanning, fixed by copper sulphate. Catechol and mixed tannin show higher values on fixation by copper sulphate both by intermittant and repeated tanning; the effect is inferior when potassium dichromate is used. Even though Koura (op. cit) and Radhalekshmy and Kuriyan (op. cit) hold that dichromate is more effective for cutch (catechol group), the present studies tend to show that copper sulphate is comparatively more effective than dichromate. It is likely that this may be due to the difference in the relation between tannin to non-tannins which has got a practical bearing on the fixation of tannin as stated by Thorpe (1946).

3. Regarding the method of application, intermittant tanning and fixation both by copper sulphate and potassium dichromate affords better protection from rotting than repeated tanning and fixation.

4. It is evident that the concentration of tannin bath when changed to double, in general, has no special advantage over 1% tannin for initial treatment and 2% for secondary step.

Recommendations

The effectiveness of tannin fixation can considerably be enhanced by following technique. The pliability, strength and stretch of the twines were found to be unaffected by the process and the increase in weight by fixation is within limits only. On considering the cost and labour involved to retan the net at every fortnight, it will be highly ecnomical also if the fixation of tannin is followed.

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