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The Preservation of Fishing Nets by Treatment with Copper Soaps and Other Substances. Part III.

By

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It is over five years since Part II appeared and the method of testing preservatives by placing netting in jars filled with Aquarium tank water has been continued and final results obtained for those samples still under observation when the last report was written. The water in the jars was changed three times a week. At intervals tensile tests were made on the specimens by means of a spring balance and hand tests were made in general every week upon those that appeared to be weakening. In addition to the jar tests, treated netting was immersed under Plymouth Pier, where the tide runs strongly, where there is considerable wave action and where the water is at times contaminated with sewage. Here the nets were out of the water about four hours at each tide. Netting was also exposed in a tidal basin at Pier Cellars, Cawsand, just outside Plymouth Sound Breakwater. These samples were always wholly immersed.

PRESERVATIVES AND THEIR APPLICATION.

(a) Coal distillation products.

Crude gas-works benzene, used as a solvent for copper soaps; this blackens iron vessels.

Motor benzene, purer solvent, Anglo-American Oil Co.

Creosote oil, purchased locally.

Coal tar from local gas-works; a very thick tar, becomes moderately dry in one month.

Coal tar, "Corroid tar," specially prepared for nets by Messrs. Hardman, Hull; a less viscous tar, becomes moderately dry in a fortnight.

(b) "Coalite" low temperature distillation products.

Crude phenol, b.p. 180-230° C., a dark mobile liquid.

A neutral oil, b.p. 170–230° C. ("oil A"). Does not darken much on standing; has been extracted with alkali and with acid; kindly presented

by Prof. G. T. Morgan, Director Chemical Research Laboratory, Teddington, as was also "oil B."

Oil B, b.p. 225–250° C. at 14 mm. pressure, extracted like oil A.

Coalite neutral oil, b.p. 100–245°; sp. gr. 0.971; alkali extracted, darkens on standing. Presented by Coalite Works, Gawber, Yorkshire, as were also other samples.

Coalite heavy neutral oil, b.p. 220–370°; sp. gr. 0.975; alkali extracted.

Coalite middle oil, b.p. 180–320°, with 47% crude tar acids ; sp. gr. 0.966.

Coalite heavy oil, b.p. 230–280°, with 39% crude tar acids ; sp. gr. 1.018.

Coalite low temperature tar, dries moderately in about three weeks, rather quicker than the more viscous local tar; all drying rates are approximate and vary with the conditions.

(c) Wood distillation products.

Stockholm tar, from coniferous wood (softwood). A tar of low viscosity and pleasant odour, dries in about a week. It is good, but cost is somewhat high.

"Shalco" tar, a hardwood tar of moderate viscosity prepared by Messrs. Shirley Aldred, Worksop; becomes fairly clean and dry in five days.

"Shalco" oil, a yellowish tar oil, b.p. 150–270°.

" Shalco " tar, export quality, contains copper resinate blended with it. Resin spirit, sp. gr. 0.883.

Resin spirit, sp. gr. 0.930.

(d) Petroleum products.

White spirit is a distillate (Shell Co.) between $140-200^{\circ}$; it is of low flash point.

Kerosene or paraffin oil (Shell) distils at 150–300°; it has a higher flash point being prepared for domestic use.

Petrol, as for motor cars, Anglo American Oil Co.

Lubricating oil, Shell Mobiloil A.

(e) Cutch varieties.

Cutch from The Bakau and Kenya Extract Co., probably a mangrove extract, but the company's representatives in Glasgow refused all information; sold as Caller Herrin Brand.

Forestal brand cutch, from the heart wood of the South American Quebracho tree, *Quebrachia schinopsis lorentzii*.

Elephant brand extract, from the bark of the South African mimosa

or black wattle, *Acacia decurrens* var. *mollissima*. These have approximately the following composition and are completely soluble in hot water.

	M	imosa extract.	Quebracho extract.
Soluble tannins (cold water) .		62.5	63.4
Soluble non-tannins (cold water)		19.5	8.3
Insolubles (cold water)		0.3	8.0
Water		17.7	20.3
		100.0	100.0

The "insolubles" are soluble in hot water. These two samples and analyses were kindly supplied by the Forestal Land, Timber and Railways Co.

(f) Copper compounds.

Copper sulphate, crystals, commercial quality. For Olie's method use a 1% solution in water and add just enough ammonia solution to redissolve the precipitate first formed; this requires about 44 volumes of ammonia solution (sp. gr. 0.88) for 1000 volumes of copper solution; the result is a deep blue solution; it is used after cutch. Soak 10–15 min.

- 1. Mixed copper soap, containing stearate with oleate, palmitate and laurate; made by Lever Bros. (Messrs. Ogston and Tennant's "Pilot Protective Copper Soap"). This is a dark green greasy solid, rather less soluble in petrol than is the oleate. For use with nets it is prepared to contain about 20% of creosote or of thick mineral oil. It appears to be rather more effective as a preservative than oleate alone. We are indebted to Lever Bros. for a number of samples.
- Copper oleate, a dark green greasy solid. Use and properties very similar to the foregoing. Obtained like the resinate from Messrs. Wm. Bailey & Sons, Wolverhampton; the firm kindly provided a number of samples. The oleate contains about 2% of added creosote.
- 3. Copper resinate, a light green dry powder, clean to handle ; not very soluble in petrol, soluble in benzene, solvent naphtha and in oil A (neutral low temperature tar distillate).
- 4. Copper naphthenate, a dark green greasy solid, sold for use in solvent naphtha or various petroleum oils. It is on the market as "Cuprinol" of various grades; formerly made in Denmark, it is now made in England also. As a result of tests done here a certain proportion of coal tar is now incorporated with the quality sold for nets. The samples of the Danish and British products were kindly presented by the Companies. The "colourless Cuprinol for ropes" is the corresponding zinc salt; the "brown Cuprinol" contains the iron salt.

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Copper naphthenate is also the basis of the Shell Canvas Preservative, and Shell Wood Preservative, which also contain paraffin wax and petroleum distillates, such as white spirit, kerosene or gas oil. Samples were kindly presented by the Company.

FINAL RESULTS OF TESTS REPORTED IN PART II.

When Part II appeared (this Journal, 1930, Vol. XVI, pp. 583–588) nets which had received certain treatments were still sound. The further results are given in Tables 1 and 2, from which it may be seen that the preservation of nets by Olie's method is a great advance over cutch alone. It is cheap, simple and where the nets can be re-treated at appropriate intervals it gives good results. Among the copper soaps the mixtures of both copper oleate and of copper naphthenate solutions with coal tar are very good, and a single treatment may last a long time.

TABLE 1.

(Table 2 of Pt. II, final results.)

Cotton net rotting in Aquarium tank water ; initial strength, dry, 18 lb. Immersed 20/10/26. Untreated lasted 5½ months.

Treatment.					Re-treatments.	Time till rotten, in years.
Cutch, two boilings					Every two months	11
Do					Every three months	$2\frac{3}{4}$
Do. and Olie's ammo	onia	coppe	r sulp	hate	Every four months	$6\frac{2}{3}$

TABLE 2.

(Tables 12 and 13 of Pt. II, final results.)

Hemp and cotton netting rotting in Aquarium tank water or in tap water. Initial strength, dry, hemp $16\frac{1}{2}$ lb., cotton $18\frac{1}{2}$ lb. Immersed 25/11/26.

//		Time till rotten, in years.					
		Her	mp.	Cotton.			
Treatment.			Salt	Fresh	Salt	Fresh	
			water.	water.	water.	water.	
Mixed copper soaps, 10% in petrol .			1	$3\frac{1}{2}$	1	6	
Do. with coal tar, 10%			$3\frac{3}{4}$	4	$3\frac{1}{2}$	$6\frac{3}{4}$	
Cuprinol (Danish) with equal vol. of petrol			31	2	4	$6\frac{1}{2}$	
Do. with coal tar, 10%			33	8	41*	81	
Equal volumes of mixed copper soaps and C	Jupri	nol			-	~	
as above (viz. diluted)			$3\frac{1}{2}$	8	$2\frac{1}{2}$	$7\frac{1}{4}$	
* Still 9 lb jar missing							

* Still 9 lb., jar missing.

FURTHER TRIALS OF NET PRESERVATIVES.

In the light of the experience already gained a large number of trials were made with the object more especially of testing different varieties of cutch, of trying Cunningham's cutch bichromate method which is still

largely used and of testing various tar products. Above all it was desired to combine copper soaps with different organic solvents and tar with a view to cheapening and, if possible, still further improving these mixtures, which had already given very good results.

Table 3 shows that Olie's method is effective on three cutch extracts, very different in origin ; compared with the advantage of using Olie's method the differences between the preservation afforded by the extracts alone become insignificant.

TABLE 3.

Cotton netting rotting in Aquarium tank water; initial strength 20 lb., dry. Two boilings in cutch, alone or with Olie's treatment.

			Life of net in months.		
			Alone.	Olie's method.	
Untreated control .			2	2	
Cutch, mangrove (?)			8	16	
Quebracho extract			8	18	
Black wattle extract			9	16	

Olie's method appears to be much used by the Dutch, but is unfortunately never used in this country. It was introduced in 1917. When retreating a net according to Olie's process it is not enough to dip again in the ammoniacal copper sulphate, but the net must have two boilings in cutch and then the blue dip. A net which received re-treatments of the latter only failed after 20 months as against over six years for the complete re-treatment.

CUTCH AND LOW TEMPERATURE TAR PRODUCTS.

Table 4 shows the value of certain low temperature tar products alone or after cutch. Oil A is volatile; oil B leaves the net somewhat messy, but is cleaner than tar. The low temperature tar is of relatively low viscosity as compared with ordinary gas works tar.

TABLE 4.

Cotton net as in Table 3, with similar cutch treatment, alone or with tar product.

						Life of net	in months.		
						Tar product.	Tar product after cutch.		
Neutral tar oil A						13	14		
Neutral tar oil B						15	54+*		
Low temp. tar						54 + †	54 + 1		
Untreated control						$2\frac{1}{2}$	$2\frac{1}{2}$		

* Strength still 17.3 lb. † Strength still 18.6 lb. ‡ Strength still 10.8 lb.

CUNNINGHAM'S CUTCH BICHROMATE METHOD COMPARED WITH COPPER SOAP MIXTURES.

Cunningham's book, which is out of print, advises the use of a bichromate solution after two boilings in cutch. It directs that the net should be placed in, or passed through, a previously boiled $2\frac{1}{2}$ per cent solution of potassium bichromate. "The best way is to pass the net through, adding more hot bichromate from time to time, as the hotter and cleaner the bichromate solution is, the better it will act."... "The bichromate should not be used more than once a year, or once at the beginning of a season. During a season the nets are to be boiled—that is cutched—in the usual way, but not so often."

At the outset of the net tests here this method was omitted because Dr. Olie must have known of it and introduced the ammoniacal copper sulphate method as superior. Taylor and Wells also tried it and rejected it. As, however, it is largely used still in England we have tried it. It is apparently a method that may or may not prove a success. One of the leading net preserving firms once showed me netting thus treated which had quite inexplicably rotted.

TABLE 5.

Cotton herring netting, cotton $36^{s}/9$ -ply, rotting in Aquarium tank water ; strength at start 5.3 lb.

			Breaking load.	Time elapsed, months.
Untreated control			0	2
Cunningham's cutch bichromate applied by net	make	ers	0	$7\frac{1}{2}$
Copper resinate 10%, coal tar 10% in benzene			3	18
Copper oleate 10%, coal tar 10% in benzene			6.0*	24
Danish Cuprinol			3	24
Danish Cuprinol with 10% coal tar			4.7	24
Untreated control, warmer weather series .			0	1
Cunningham's cutch bichromate applied by net	mak	ers	0	5\$
Copper resinate 10% in benzene			0	$5\overline{\frac{5}{2}}$

Table 5 shows that even when carried out by an experienced firm the cutch bichromate method is not nearly as effective as the copper soap and tar mixtures. Moreover, the latter leave a pliable net and cause no shrinkage, whereas cutching hardens and shrinks the net with each successive re-treatment. To avoid slipping of the knots with the copper soap and tar mixtures they may, when new, be hand tightened or may be given an initial short boiling in cutch. According to Filon this is an advantage.

* Slightly stronger than initial strength of untreated net, probably due to local variation in the twines or possibly to the cementing action of the tar.

PRESERVATION BY MEANS OF COPPER SOAPS WITH WOOD AND COAL TAR DISTILLATES.

Several series of tests have been combined in Table 6; a few combinations with tar are missing owing to the disappearance of the jars. It may be seen how greatly the tar products are improved by having a copper soap added, also that solutions of the latter are much improved by having 10% of a tar added.

TABLE 6.

Cotton netting rotting in Aquarium tank water; strength when new 20 lb., dry. The figures denote the life of the netting in months, or the time when the final examination was made; for strengths then see footnotes. Untreated controls lasted about $2\frac{1}{2}$ months.

Tre	atme	nt.			Tar product, alone.	Copper oleate, 10% in petrol.	Copper resinate, 10% in benzene.	Cuprinol.
Hardwood oil b.p.	150-	270°	C. (Sł	nalco)	10			
Hardwood tar (Sha	lco)				22	50^{*}		
No tar					_	24†	29††	54±
Crude phenols					5	2211		4
Neutral tar oil A					13	3611		
Neutral tar oil B					16	46İİ		
Low temperature t	ar				53§	53 ±±		
Coal tar, Plymouth	1				36§§	3688		
Coal tar, Corroid					36§§	36§§	49‡‡**	

The tar and copper soap mixtures are very good. These mixtures were prepared by adding the tar to the hot melted copper soap. Where a solvent was also used the warm mixture was then poured in with stirring. The object of using the solvents is that the 10 per cent copper soap, with 10 per cent tar in a solvent, is far lighter and cleaner to handle than are copper soap and tar mixtures. The cheapest solvent, and the best, as shown by the tests on ropes in the accompanying paper is the neutral tar oil, low temperature process; either oil A or the closely similar product extracted with alkali only may be used. Oil A, with copper resinate or with copper oleate gives a pliable net, very clean to handle and having an attractive green appearance. Oil B is rather messy alone,

* Blended with tar by the makers, no petrol. † A hemp net lasted 28 months, its control 3³/₄ months; initial strength 18 lb., dry.

Original strength maintained, also in a hemp net.

§ Still strong, average 18.6 lb.

Strength 6.6 lb.
Had 10% of the tar product in oleate solution.
Only 22 months in solvent naphtha.
** Strength still 8.2 lb.

§§ Strength still 17.0 lb., Plymouth tar; 21 lb. Corroid tar; Plymouth tar-oleate mixture 13.7 lb.; Corroid tar-oleate mixture 17.2 lb.

but with copper soap and petrol in the proportions given it is considerably less messy than tar used similarly. In the pound, pound and gallon* proportions the tar even is tolerably clean to handle, especially when copper resinate is used instead of oleate.

Solutions of copper resinate in resin oil with or without added resin, or diluted with petrol all proved unsatisfactory; they gave sticky nets which lasted in the three cases tried just 19 months, whereas a control with copper oleate alone in petrol was still well above half-strength after 21 months.

It also seemed desirable to compare the various types of "Cuprinol" now on the market and the original Danish product. Strong cotton net, $32^{s}/30$ -ply, was again used, and the pieces averaged $17\cdot0-19\cdot0$ lb. when new and treated. The material was soaked in each mixture for the usual 15 minutes, though less would probably have sufficed on account of the good penetration of Cuprinol. The series comprised : No. 131A, green Cuprinol for nets, British made and containing a proportion of added tar ; No. 132A, brown Cuprinol for nets—this is an iron naphthenate ; No. 133A, colourless Cuprinol for ropes, a zinc naphthenate ; No. 134A, untreated control and No. 135A, Danish green Cuprinol, the copper salt, without tar. The control perished in 4 months. After 29 months the strengths were, in order, 19.6, 15.0, 17.8, 0 and 20 lb. Green algæ were growing on the zinc naphthenate net. The tests are still in progress, but other experiments with ropes are strongly in favour of the green (coppercontaining) Cuprinol with tar.

THE PRESERVATION OF SILK PLANKTON NETS.

These nets, made of bolting silk of mesh from 200 to the inch for the finest to 25 to the inch for the coarse, are costly and liable to damage at sea, especially once they have become weakened. It was established that it was deleterious to rinse in fresh water after use, or to disinfect periodically with formalin. Exposure to sunlight was found to be a potent source of deterioration. For many years now it has been the practice at this laboratory to treat the nets with a copper soap solution. First of all copper oleate was used with good results, but it was hard to secure an even treatment since sizing prevented the penetration of the soap. Washing in "Lux" was not found to effect any very marked improvement in removing the sizing. Then copper resinate was used for a while as nets so treated were a uniform light green, but they had a tendency to be somewhat stiff at first. Finally green Cuprinol was used; it gives a uniform colour and leaves the net pliable. As the present issue for nets

 \ast 1 lb. of soap and 1 lb. of tar to 1 gal. of solvent gives approximately a 10% solution for soap and for tar.

has some tar we tried diluting it to avoid blocking of the meshes and to cheapen the process.

Furthermore a series of tests was made in which portions of 200-mesh netting were treated according to the various methods and placed in jars to rot. As a result it was established that by far the best treatments as regards durability were: (a) green Cuprinol undiluted; (b) green Cuprinol with tar, as sold, with equal volume of petrol and (c) the same with three of petrol to one of Cuprinol. The last-named treatment is not costly either in view of the value of the nets. With Cuprinol at 9s. per gallon and with petrol at 1s. 3d. per gallon, the 25 per cent mixture comes to 3s. 2d. per gallon as compared with the copper oleate solution in benzene, 3s. 6d. per gallon, or in petrol, 2s. 9d. per gallon. The three Cuprinol treatments mentioned prolonged the life of the net to about 11 months of continuous immersion, as against $3\frac{1}{2}$ months for the untreated net; even $3\frac{1}{2}$ months is an unusually long life for this fine mesh, as earlier tests gave about one month.

Thus on the score of durability, pliability, freedom of blocking of the mesh, and of cost, the dilution of the green Cuprinol for nets with three volumes of petrol is recommended as the best treatment for silk nets. As however copper oleate is sold in solid form it may be more conveniently sent by post and quite good results are obtainable with it. Probably a mixture of equal volumes of oleate and of resinate solution would behave well, but we have no extensive experience of it.

Shell canvas preservative and Shell wood preservative were also tried for silk nets, since in them the basis is also copper naphthenate. Neither proved satisfactory, probably on account of the large amount of paraffin wax present.

TESTS ON NET PRESERVATIVES IN THE SEA.

With the results already obtained as a basis, sixty-five pieces of netting were placed below the Plymouth Promenade Pier where the rope tests were conducted. No information was obtained from this since the pieces of net fouled the supports and barnacle-covered girders. Within a month they were torn to pieces. Duplicate sets were then suspended from ropes slung across the laboratory's fish pond at Pier Cellars, Cawsand, just outside Plymouth Sound Breakwater. This basin never becomes dry, but is completely filled and more than half-emptied again each tide.

The methods tested were as follows: cutch, Olie's, Cunningham's, coal and wood tars, neutral low temperature tar oils and creosote, varieties of Cuprinol, Shell canvas and wood preservatives, copper oleate, copper resinate and a series of tests with these and different solvents such as petrol, paraffin oil, benzene and tar oils, total 64 and one control. The netting was cotton $32^{s}/12$ -ply, 100 mesh deep, 26 rows to the yard, initial strength 7 lb. per thread.

The water being very clean, the untreated netting took $5\frac{1}{4}$ months to become rotten, and treatment with Coalite oil A did not prolong its life. Cunningham's cutch bichromate method was tried in three ways, since no exact times or temperatures are specified in the description quoted. When the net was placed in boiling bichromate for 5 minutes it was rotted at once; leaving it in bichromate, cooling down from boiling, for 5 minutes gave a net lasting 7 weeks only, and soaking for one hour in cold bichromate gave exactly the same result. Two boilings in cutch without bichromate lasted $3\frac{1}{2}$ months only, though our jar tests showed that cutch had a preservative action.

The duplicates were slung on different ropes, there were four ropes in all, so that the effects of chance local conditions might be eliminated. Nevertheless, seaweed collected in places and soon rotted nets, the duplicates of which remained sound. With these exceptions all the treatments were found to keep the netting sound from May 15th to November 8th, 1934. When examined again on November 22nd it was found that almost all had become rotten. It was also observed that up to November 8th the bottom of the basin was covered with Laminaria etc., whereas on November 22nd the bottom was devoid of seaweed and remarkably clean, yet on the rocks outside the seaweeds had continued as usual. It appears that the large amount of rotting seaweed must have made the water so foul as to subject the nets to very heavy bacterial infection. It was noticed that many of those containing copper compounds had become black owing to the formation of sulphide; the low solubility of the latter renders it practically non-toxic.

The nets which had rotted included specimens treated, by one of the best makers, according to Cunningham's method. The five remaining out of the two sets of 65 each included No. 61, copper resinate 1 lb., "Corroid" tar 1 lb., Coalite oil A 1 gallon; this lasted a little longer, up to $6\frac{1}{4}$ months. No. 37, copper resinate 1 lb., to 1 gallon "Coalite" low temperature tar, lasted 8 months; No. 36, copper resinate 1 lb., Corroid tar 1 gallon, lasted 9 months. In all three cases, however, only one of the duplicate samples remained sound. Only No. 29 remained in duplicate, one lasting 7 and the other 8 months; the treatment was green "Cuprinol" with tar added, the British product. The other copper naphthenates, "Shell" products, had gone.

There is no doubt that the ones which did remain are good, but one is not at all sure that the conditions were always comparable, on account of the draping of the loose seaweed along the nets. As a whole, this large series gave less information than had been expected, but the relative merit of the treatments is better shown in the following paper in which they were applied to ropes, which were immersed beside the nets simultaneously.

THE PRESERVATION OF TRAWL NETS.

These nets are very commonly used without any preservative in England, on the score that they are in any case liable to damage by tearing. They are, however, made in sections, and commonly only the lowermost of these gets torn. Furthermore, though even new trawl nets may get caught in an obstruction and be badly damaged, yet in many cases tears occur only after considerable use when the net has already become much weakened through rotting of the twine. Were new nets to tear thus, the obvious way of meeting the difficulty would be to use stronger twine, and this would have been done long ago. The alternative is to maintain the twines now used as near as possible at their original strength by proper preservatives.

Some tests were carried out with twines supplied by the Advisory Committee on Vegetable Fibres to ascertain whether certain fibres produced within the British Empire were as suitable as manila for use in trawl nets. The small amount of material available was made up into netting in order to see whether the bending at the knots was a potential source of weakness, also to test the penetration of the preservatives into the knots. No evidence was obtained of failure at the knots.

The fibres used were sisal (Agave sisalana Perr.), New Zealand flax (Phormium sp.), and Benares sann hemp (Crotalaria juncea L.). The twine all averaged well over 100 lb. when new. In Aquarium sea-water the untreated controls were rotten in about $5\frac{1}{2}$ months, rather less for the sann hemp. This treated with the usual mixture, copper oleate 1 lb., coal tar 1 lb., petrol 1 gallon, lasted for 8 months, whereas the sisal lasted for 24 and the Phormium fibre for 29 months. It was obvious that none of the twines had been properly penetrated in a ten minutes' dip, which was unfortunately the treatment. Far better results should be obtainable with longer soaking which is necessary for these hard fibres, though unnecessary for cotton.

The results obtained with Olie's method were, however, extraordinarily good. Sann hemp and Phormium fibre lasted 34 months, and the sisal twines still averaged 12 lb. after 48 months—and this with a single initial treatment.

The matter was not pursued further, but it is highly probable that Olie's method followed by a dip in one of the tar oils or in tar would give very good preservation indeed. There is some objection to the use of tar in quantity owing to cases of tar cancer having occurred. It is quite possible that the double washing, in alkali and in acid, used in producing the neutral oils, may remove the carcinogenetic substances, so that oil B could be used instead. It is less messy than tar. In any case, Olie's method alone is very good.

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FISHING LINES.

A few tests were carried out upon lines for use with rods, sold as cotton, flax, silk and enamelled silk. Some unsatisfactory attempts were made to use the copper preservatives, but this was before the addition of tar improved the adherence of the preservative.

A solid braided green translucent silk fishing line remained fairly sound in both tap and Aquarium salt water for three months, but had perished inside four. In this case the application of a mixed copper soap (oleate, stearate, palmitate) was useful, for the line was fairly strong after four months in salt and after five in fresh water.

A plaited pure flax line remained sound in tap water for five months, but became absolutely rotten in sea-water in one month.

A fine Japanese silk line or artificial gut, dyed brown, was easily broken after one month in fresh water. A somewhat stouter Japanese silk line, undyed, also broke readily in one month, and had completely disintegrated in less than four. Another sample tested was Japanese silk worm gland line, obtained by drawing off the silk by hand from the gland; the major portion of this line is translucent. After one month in fresh water this sample could be broken with some effort, but even after three the centre portion was quite sound, the breaks being at the ends. After five months the broken centre pieces were still fairly strong. It is thus much superior to the woven silk. For these three samples and for the information concerning their preparation I am indebted to Dr. Ikusaku Amemiya of the Imperial University, Tôkyô.

Good results were obtained with a thin green dyed line, sold as "Justice Brand plaited silk line." On enquiry it was found that this was made by Messrs. Tubb, Lewis & Co. of Wotton-under-Edge. The firm kindly presented a number of samples for testing. The plaited cotton lines averaged 13.5, 20.4, 25.0 and 29.6 lb. when new; they became rotten after 4, 5, 6 and 8 weeks respectively in the jar tests with Aquarium water. The first and third were dyed yellow, the other two dark green, but the dye seems to have had no preservative action. Five samples of plaited flax line were tested; these when new averaged 17.4, 28.5, 32.6, 41.7 and 47.0 lb. The first, third and fourth were brown, the second and fifth green. These flax lines perished in 6, 8, 5, 5 and 8 weeks respectively, but the two that lasted 8 weeks were green dyed, so this dye may have had some favourable action. In all this set of tests the lines were soaking in approximately twenty times their own weight of water. The seven lines denoted as plaited silk were in comparison outstandingly good, though usually silk becomes rotten quite soon in sea-water. The initial strengths were 5.2, 8.0, 15.6, 18.5, 21.8, 25.2 and 33.5 lb.; of these the first, fourth and fifth were drab, the others white. They lasted $6\frac{1}{4}$, 6, 5, 8,

 $3\frac{1}{2}$, $3\frac{1}{2}$ and 8 months respectively, whereas none of the cotton or flax lasted more than 8 weeks. Obviously the green dye in the first sample of Justice Brand plaited silk line, purchased locally, had nothing to do with its resistance to decay.

It is obvious that these tests in which the lines are left soaking in water do not represent actual conditions for rod lines; they are, however, of comparative value. Furthermore, it must be remembered that, if even slightly damp, rotting goes on; some bacterial deterioration takes place even in the "air dry" condition. There is therefore a use for the copper soap preservatives in these lines also, to which they should be applied in weak solution and soaked to secure good penetration.

TESTS FOR COPPER AND ZINC SALTS AS PRESERVATIVES.

An approximate idea can be gained as to how a preparation containing salts of the above metals is likely to behave as a preservative by means of sodium diethyldithiocarbamate. A trace of the reagent gives a golden yellow-brown with copper, a darker brown with iron and a white with zinc, and these reactions are extremely sensitive.

With copper oleate it may be seen that copper is given off more freely than with copper resinate, hence the latter lasts longer. On the other hand copper naphthenate (Cuprinol) is a far more active source of copper ions; it is only on account of its higher concentration owing to its solubility in petroleum products and its excellent powers of penetration that it lasts as well as it does. Zinc naphthenate is even more active, but the ions are less toxic. The beneficial effect of added tar is largely due to the fact that it diminishes the rate at which copper ions are given off; they may thus continue to diffuse out long after the tar has lost its own toxic compounds.

Nets which remain sound after long immersion are found to be giving off appreciable amounts of copper or zinc ion, whereas those which are much weakened give off little or no copper or zinc.

SUMMARY.

1. Frequent treatment with cutch is injurious, but Olie's method (cutch and ammoniacal copper sulphate) applied every four months preserved cotton netting for six years and eight months in Aquarium sea-water.

2. Varieties of cutch tested showed differences which were quite insignificant in comparison with the improvement effected by adopting Olie's method, which was effective with all on cotton.

3. A single treatment by Olie's method preserved trawl twines of Benares sann hemp, New Zealand Phormium fibre and of sisal (E. African) for 34, 34 and more than 48 months respectively under conditions such that the untreated twines perished in less than five months.

4. Cotton treated with cutch alone is but little improved by a dip in crude phenols, but a neutral tar oil obtained from the "Coalite" low temperature distillation process was found useful.

5. Cunningham's treatment with cutch and bichromate is not easy to get exactly right and the best results of net makers seem far inferior to those obtained with Olie's method or with copper soaps and tar.

6. Copper soaps dissolved in benzene, petrol, etc., may be arranged thus in order of effectiveness, but the first three are not very different in durability.

- (a) Copper oleate.
- (b) Mixed copper soaps (Lever Bros.).
- (c) Copper resinate.
- (d) Copper naphthenate (Cuprinol), best by far.

7. The addition of tar to the copper soaps brings them more nearly level. Effective mixtures contain 1 lb. of oleate, mixed soaps, or resinate, 1 lb. of coal tar to 1 gallon of benzene or petrol (save for resinate). Cuprinol as now sold for nets has tar incorporated by the makers. Single treatments with such mixtures have preserved cotton netting up to $3\frac{1}{2}$ years under conditions which brought about the decay of untreated netting in 2–5 months, according to season and state of the water.

8. A very effective and cheap dip may be obtained by replacing the benzene or petrol in previous paragraph by "oil A," a neutral oil from "Coalite" process, b.p. $170-230^{\circ}$ C. This is a good solvent for copper resinate, and if solvent is a non-darkening grade, resinate without tar gives a clean light green net; but the greasy nature of oleate and naphthenate is probably an advantage.

9. For hard use and where the extra weight is unimportant coal tar, hardwood tar (Shalco) or softwood tar (Stockholm tar) may be used; a specially prepared coal tar (Corroid tar) is particularly good, also "Coalite" tar.

10. These tars are all greatly improved by the addition of a copper soap, 1 lb. per gallon. In a tidal basin copper resinate with Corroid tar or Coalite tar and Cuprinol made with tar were all found to be very good.

11. Bolting silk plankton nets may be preserved by treatment with copper oleate or copper resinate in benzene, without—or with very little —tar. The most effective treatment, however, is to use a dilute solution of copper naphthenate with tar; this is obtained by diluting "green

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Cuprinol for nets " as now made in England, with three volumes of m otor car petrol.

12. Cotton and flax fishing lines for use on rods were found to become rotten in 4–8 weeks in Aquarium sea-water, but their durability can be improved by soap and tar solutions in benzene. Japanese silk gland (hand drawn) line is rather better than untreated cotton or flax, and a solid braided green translucent silk line lasted for 3 months. Best of all tried here were lines marketed as "Plaited Silk, Justice Brand" (Messrs. Tubbs, Lewis & Co.), which under similar conditions to the others lasted from $3\frac{1}{2}$ to 8 months.

13. A rough idea of the serviceableness, as a preservative, of a copper or zinc soap can be obtained by testing the material treated with salt or fresh water to which a trace of sodium diethyldithiocarbamate is sub-sequently added. This will show the rate at which traces of copper (golden yellow) or of zinc (white) are being given off; the test may be applied to freshly treated samples or to those which have had long immersion.