

## The stability, staining and corrosive properties of an iodine-non-ionic surface-active agent complex

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The stability of concentrated and dilute solutions of an iodine-cetomacrogol complex and the staining of fabrics and the corrosion of metals it produced, have been compared at the same available iodine concentration, with a system based on weak iodine solution B.P. The available iodine content of the complex decreased on storage, but this loss was associated with the production of an equivalent amount of hydrogen iodide, such that the total iodine content of the system remained constant. The reaction was accelerated by an increase in temperature, but was neither a photochemical nor an oxidative decomposition. The complex was not subject to the large losses of solvent which occurred with the potassium iodide-ethanol system, and in dilute solution was generally more stable; both systems being more stable in acid conditions. Dilute solutions of electrolytes, as found in hard waters, had little effect on the stability of either type of dilute solution except where they caused the pH to rise, but potassium salts produced a characteristic precipitation of the complex, which resulted in a loss of available iodine. The technique of testing the permanency of staining indicated that the complex often produced the less permanent stain, but it was not completely devoid of staining properties. The complex was less corrosive towards certain metals when tested by a static total immersion test, but when the attack was severe as with aluminium and copper, there was little difference between the two iodine systems in their corrosive action.

AMONGST the advantages claimed for iodophors are increased stability, especially in dilute solution, and decreased staining of fabrics and corrosion of metals (Lazarus, 1955, Wetzler, 1959; Wilson, Mizuno & Bloomberg, 1961). The work reported in an earlier paper has shown that an aqueous iodine system can be prepared by addition of cetomacrogol 1,000 B.P.C. The stability, staining of fabrics and corrosion of metals of such a system has been compared with weak iodine solution B.P. Both systems contained the same amount of available iodine.

### Experimental

The limits of the amount of iodine which can be incorporated into an aqueous solution of cetomacrogol are set by the solubility of iodine in the cetomacrogol solutions and the concentration at which cetomacrogol solutions form a gel. Thus, allowing for batch variation, an aqueous system containing 2% iodine can be prepared in a 20% solution of any of the three batches of cetomacrogol described in an earlier paper (Hugo & Newton, 1963).

The iodine-cetomacrogol system was prepared by melting the cetomacrogol (batch C) in a closed vessel at 50-60°, adding finely ground iodine and agitating until all the crystals of iodine had disappeared, this taking 2 to 3 hr. Water at about 50° was then added with constant agitation to disperse the gel which formed. Final adjustment to volume was made when the system had cooled to room temperature. The

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analytical details of the system and of the dilution of the weak iodine solution B.P. (henceforth referred to as iodine solution) were for the complex (g/litre: available iodine, 20.32; total iodine, 23.70; HI, 3.36; iodide, 4.21; pH, 1.93. For the solution they were: available iodine, 20.08; iodide, 20.04 (KI); pH, 6.20.

#### THE STABILITY OF IODINE SYSTEMS

*Stability of undiluted solutions.* The effect of light, the protective effect of amber glass; the effect of air and of temperature were investigated after eliminating the factor of closure by storing in ampoules sealed by fusion. The effectiveness as closures of corks, aluminium screw caps with rubber liners and glass stoppers was assessed using 4 fl oz clear glass bottles to store the systems. The storage in open containers was studied by placing 10 ml of solution into a series of 100 ml beakers, weighing after known time intervals and determining the iodine content.

*Stability of dilute solutions.* In this series the stability of systems containing 400, 200 and 35  $\mu\text{g/ml}$  of iodine was estimated over a period of 80 days when contained in glass stoppered volumetric flasks and stored in darkness. Similar series were also set up but dilution was with citric acid:disodium hydrogen phosphate buffers of pH 2.2, 4.0 and 6.0. The effect of pH on the availability of iodine and stability of solutions of 2,000  $\mu\text{g/ml}$  was ascertained under the same conditions, with sodium acetate:hydrochloric acid, disodium hydrogen phosphate: citric acid and glycine sodium chloride: sodium hydroxide buffers.

*The effect of water hardness* on dilutions ranging from 5,000 to 10  $\mu\text{g/ml}$ , over 9 weeks storage in glass stoppered volumetric flasks, in darkness, was determined. Two types of synthetic hard waters were employed those of (i) Klimek & Bailey (1956) and of (ii) Kravetz & Stedman (1957).

These give a water hardness of 320 ppm calcium carbonate for (i) and 328 ppm calcium carbonate for (ii). They were used undiluted to give a final water hardness of these values and at a 1:10 dilution to give 32 and 32.8 ppm calcium carbonate.

*The effect of electrolytes* was determined qualitatively by adding equal volumes of saturated solution of the electrolyte and iodine-cetomacrogol systems and quantitatively by adding known molar concentrations of electrolyte solutions.

#### THE STAINING OF FABRICS

Two inch square pieces of selected BPC dressings were completely immersed in the undiluted iodine preparations for 2 min. The dressing was removed and allowed to drain for 30 sec, before washing by placing in 2 litres of cold water in a screw cap bottle fitted with plastic baffles to ensure turbulence in the water when the bottles were rotated at 56 rev/min. After washing for the required time, the samples were removed and dried between filter paper and examined for staining.

# IODINE-NON-IONIC SURFACE-ACTIVE AGENT COMPLEX

## THE CORROSION OF METALS

The corrosion produced by 5,000 and 100  $\mu\text{g/ml}$  iodine was investigated in both types of solution by a static total immersion test. Cleaned and degreased samples of metals of known size were suspended by a glass hook at a depth of 2 cm below the surface of the solution contained in a screw cap glass bottle. At known times the metals were removed, washed in running distilled water, rinsed in acetone, dried between filter paper and weighed. Macro- and microscopical observations were made before replacing the samples in the solution. The solutions were replaced when no iodine could be detected or when they had reached a constant low level.

TABLE 1. METALS USED IN CORROSION TESTS

Metal	Source
Galvanised mild steel .. .. .	See text
Aluminium .. .. .	B.D.H. reagent grade foil
Copper .. .. .	B.D.H. analytical reagent grade foil
Nickel .. .. .	B.D.H. reagent grade foil
Tin .. .. .	B.D.H. " " "
Tin and lead alloy .. .. .	B.D.H. " " " 50% tin and 50% lead
Lead .. .. .	Commercial sheet supplied by the Metallurgy Department of Nottingham University
Mild steel } .. .. .	Supplied by the Metallurgy Department of Nottingham University
Zinc } .. .. .	
Stainless steel } .. .. .	
Monel .. .. .	Monel Nickel Co. Ltd., 63% nickel and 28-34% copper

The metals tested are listed in Table 1. The galvanised mild steel was prepared by cutting, drilling, cleaning, degreasing and drying a sample of mild steel of the required size. After coating with a flux (consisting of 70% zinc chloride and 30% ammonium chloride made to a paste with water) and drying in a bunsen flame, the sample was immersed in molten zinc, at 500° removed, drained and cooled before smoothing the surface with OO emery paper. The film was 0.03 mm thick.

## Results

### THE STABILITY OF THE IODINE SYSTEMS

The iodine and hydrogen iodide content and pH of the iodine systems after 52 weeks storage under varying conditions is given in Table 2.

TABLE 2. THE EFFECT OF STORAGE CONDITIONS AFTER 52 WEEKS ON THE STABILITY OF IODINE PREPARATIONS

Type of glass	Sealed under	Temp.	Conditions of light	Iodine-cetomacrogol complex			Iodine solutions		
				Iodine conc. g/litre	Hydrogen iodide conc. g/litre	pH	Iodine conc. g/litre	Hydrogen iodide conc. g/litre	pH
Clear	Air	Room*	Daylight	17.88	5.87	1.68	20.11	—	4.66
"	Nitrogen	"	"	18.03	5.95	1.70	20.25	—	4.66
Amber	Air	"	"	17.95	5.92	1.72	20.17	—	4.66
Clear	"	"	Darkness	18.14	6.02	1.64	20.17	—	4.67
"	Nitrogen	"	"	18.14	5.78	1.72	20.38	—	4.51
"	Air	4° C.	"	18.68	5.75	1.66	20.20	—	5.04
"	"	37° C.	"	15.67	8.44	1.52	19.53	0.76	3.06

\* 14-30°

Temperature is the factor producing the greatest effect, although there was a reduction in the iodine content of cetomacrogol systems under all conditions of storage.

The production of acid was not due to the decomposition of the cetomacrogol alone, as no significant changes in the pH of a 20% solution when stored at 4, 37 and 50° were observed. In containers stored in daylight at room temperature (14–30°) for 52 weeks, the results for iodine concentration, hydrogen concentration and pH were similar for the three kinds of closure examined; the aluminium cap with rubber liner allowing the least loss of solvent. The % weight and iodine lost when stored in open beakers is illustrated in Fig. 1.

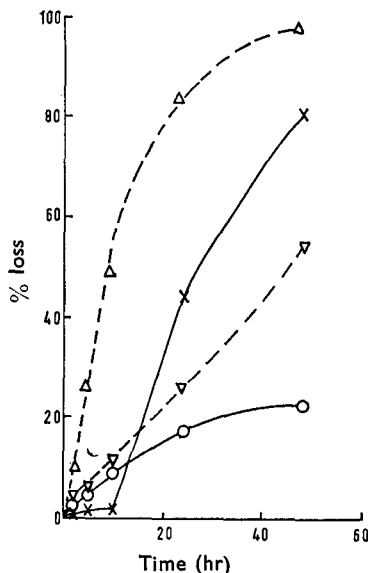


Fig. 1. Changes in the weight and iodine content of iodine preparations when stored in open beakers at room temperature.  $\Delta$  % weight of iodine solution,  $\nabla$  % weight of iodine-cetomacrogol complex,  $\times$  % weight of iodine from iodine solution lost,  $\circ$  % weight of iodine from iodine-cetomacrogol complex lost.

TABLE 3. THE EFFECT OF PH ON THE STABILITY OF DILUTIONS OF THE IODINE PREPARATIONS

Time in weeks	Iodine concentrations $\mu\text{g/ml}$							
	Iodine-cetomacrogol complex				Iodine solution			
	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
0	35.5	33.6	35.8	36.8	33.1	34.5	35.5	36.8
12	11.5	7.9	11.7	17.9	2.7	0.3	1.5	1.3
0	203.2	204.6	204.5	232.5	181.2	180.2	188.0	183.5
12	106.9	120.0	134.4	130.2	0.0	0.0	2.3	2.8
0	423.5	421.6	425.0	428.0	385.0	385.0	383.5	386.0
12	325.0	365.5	360.2	362.2	5.1	7.6	13.0	12.5

(a) no buffer, (b) pH 6.0 buffer, (c) pH 4.0 buffer and (d) pH 2.2 buffer. Solutions stored in stoppered volumetric flasks at room temperature (16–20°) in darkness.

## IODINE-NON-IONIC SURFACE-ACTIVE AGENT COMPLEX

Table 3 shows the change in iodine content of 35, 200 and 400  $\mu\text{g/ml}$  dilutions in water and in buffers of pH 2.2, 4.0 and 6.0, after 12 weeks storage in stoppered volumetric flasks, in darkness.

The effect of pH on the availability and stability of 2,000  $\mu\text{g/ml}$  dilutions is shown in Fig. 2. The iodine content of dilutions in two types of hard waters, after 9 weeks storage under the same conditions is given in Table 4. The pH of the bicarbonate-containing hard water dilutions increased as the extent of dilution increased, but never exceeded 8.0.

In the presence of electrolytes which were strongly alkaline, both iodine preparations were decolourised due to formation of iodide. In the

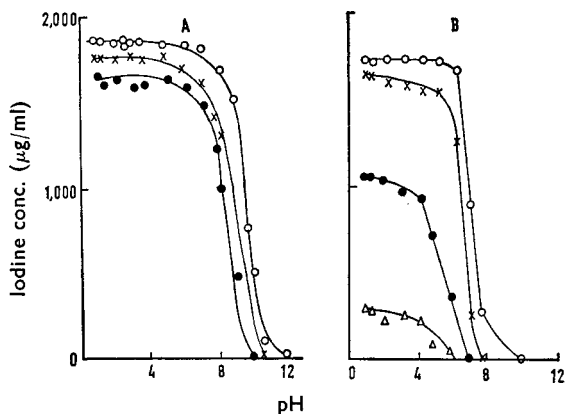


FIG. 2. The effect of pH on the availability and stability of dilutions of iodine preparations containing 2,000  $\mu\text{g/ml}$  of iodine A, Iodine-cetomacrogol complex:  $\circ$  after 0 and 5 days;  $\times$  after 58 days;  $\bullet$  after 185 days.

B, Iodine solution:  $\circ$  initial;  $\times$  after 4 days;  $\bullet$  after 38 days;  $\triangle$  after 163 days.

TABLE 4. THE EFFECT OF WATER HARDNESS ON THE STABILITY OF (A) THE COMPLEX AND (B) THE SOLUTION STORED IN STOPPERED VOLUMETRIC FLASKS AT ROOM TEMPERATURE (16–20°) IN DARKNESS

Time in weeks	Iodine concentration $\mu\text{g/ml}$				
	(a)	(b)	(c)	(d)	(e)
<b>A</b>					
0	5128.0	5128.0	5105.0	5100.0	5100.0
9	5030.0	4890.0	4900.0	4870.0	4868.0
0	1016.0	1019.0	1013.0	1013.0	992.0
9	1004.0	892.0	881.0	902.0	883.0
0	481.8	477.8	481.0	474.0	474.0
9	432.0	356.9	363.0	275.0	297.6
0	92.6	90.8	96.0	90.8	92.7
9	79.6	40.8	46.3	45.1	48.9
0	42.6	42.6	43.2	42.8	42.7
9	10.0	12.2	14.0	12.1	12.0
0	7.6	7.6	6.7	7.6	7.0
5	2.7	3.2	2.3	1.7	0.0
<b>B</b>					
0	90.7	98.9	98.9	90.0	89.3
9	74.8	76.1	78.1	5.4	0.0
0	43.1	40.9	40.5	41.2	39.2
9	36.1	35.6	33.7	0.0	0.0

(a) Distilled water, (b) and (c) water containing calcium and magnesium chlorides, to give (b) 32 and (c) 320 ppm calcium carbonate and (d) and (e) water containing calcium chloride and sodium bicarbonate to give (d) 32.8 and (e) 328 ppm calcium carbonate.

presence of potassium salts, a characteristic precipitation of the iodine-cetomacrogol complex occurred, the extent of which depended on various factors including potassium content and the iodine content of the complex.

#### THE STAINING OF FABRICS

The condition of the various dressings after the staining and washing process is described in Table 5.

TABLE 5. THE STAINING OF DRESSINGS BY IODINE FORMULATIONS

Dressing	Iodine-cetomacrogol complex		Iodine solution	
	10 min washing time	60 min washing time	10 min washing time	60 min washing time
<i>Bandages:</i> White open weave	Pale blue staining of some fibres	No stain remaining	Blue staining of fibres	Slight blue stain
Calico	Pale blue irregular stain	No stain remaining	Dark blue irregular stain	Bright blue stain remains
Domette	Bright yellow staining of the weft, and blue staining of the warp	Slight yellow stain remaining	Dark blue staining of the warp, slight yellow staining of the weft	Blue staining of the warp, light staining of the weft
Flannel	A slight brown tinge added to the original green colour	A slight yellow stain	Definite brown colouring of the original green colour	A slight yellow stain remains
Cotton crepe	Slight staining of the rubber threads	No stain remains	Brown staining of the rubber threads and slight blue staining of the cotton	A slight brown stain remains
Crepe	Bright yellow staining of the wool warp, no effect on the cotton	Bright yellow stain of the wool remains	Bright yellow staining of the wool warp, little effect on the cotton	Bright yellow stain of the wool remains
Rayon and rubber elastic	Slight brown staining of the cotton rubber yarn, but no effect on the rayon	No stain remains	Dark brown staining of the cotton and rubber yarn, and a slight brown staining of the rayon	No stain remains
<i>Absorbent gauze</i>	No stain	remains	No stain	remains
<i>Lint</i>	General pale green blue stain with a few areas coloured brown. Both colours fade on standing	No stain remains	Bright blue stain which fades on standing	No stain remains
<i>Rayon lint</i>	A few pale yellow	No stain remains	A few pale yellow	No stain remains
<i>Silk</i>	No stain	remains	No stain	remains

#### THE CORROSION OF METALS

A full description of the effect of the two strengths of the iodine systems on the different metals and the weight change/time curves for periods of 40 to 80 weeks are given by Newton (1962). Here the results have been condensed to give the corrosion rates after the initial and final sampling (Table 6).

**IODINE-NON-IONIC SURFACE-ACTIVE AGENT COMPLEX**

**TABLE 6.** THE CORROSION RATES OF METALS BY A STATIC TOTAL IMMERSION IN SOLUTIONS OF IODINE OF STRENGTH 5,000 µg/ml FOR VARYING TIMES AND 100 µg/ml FOR 280 DAYS

Metal	Rate of corrosion in mg/sq. dm/day			
	At initial sampling, at 7 days		At final sampling*	
	A	B	A	B
<i>5000 µg/ml solutions</i>				
Aluminium .. .. .	- 8.16	- 26.40	- 6.81 (91)	- 17.48 (14)
Copper .. .. .	- 168.10	- 128.40	- 107.90 (35)	- 71.52 (49)
Galvanised mild steel .. .. .	- 96.00	- 96.20	- 6.80 (434)	- 23.22 (158)
Lead .. .. .	- 42.60	+ 21.55	- 0.52 (441)	+ 0.72 (441)
Mild steel .. .. .	- 72.90	- 87.60	- 20.44 (189)	- 54.18 (119)
Monel .. .. .	- 8.63	- 60.40	- 2.84 (287)	- 37.28 (287)
Nickel .. .. .	- 75.20	- 38.85 <sup>a</sup>	- 1.17 (518)	- 43.55 (49)
Stainless steel .. .. .	0.0	- 6.59 <sup>b</sup>	0.0 (560)	- 0.34 (434)
Tin .. .. .	0.0	- 0.02 <sup>a</sup>	+ 0.08 (560)	0.0 (420)
Tin and lead .. .. .	0.0	+ 32.60 <sup>b</sup>	- 0.63 (560)	+ 1.07 (385)
Zinc .. .. .	- 179.60	- 153.00	- 2.67 (441)	- 11.73 (441)
<i>100 µg/ml solutions</i>				
Aluminium .. .. .	- 0.37	- 0.27	- 0.09	- 0.10
Copper .. .. .	+ 3.77	+ 8.38	+ 3.62	+ 6.54
Galvanised mild steel .. .. .	- 0.09	- 2.29	- 0.42	- 0.56
Mild steel .. .. .	- 6.40	- 6.90	- 4.82	+ 7.24
Monel .. .. .	- 0.67	- 0.21	- 0.13	- 0.22
Nickel .. .. .	- 1.10	- 1.42	- 0.05	- 0.54
Stainless steel .. .. .	0.0	0.0	- 0.02	+ 0.01
Tin .. .. .	+ 0.17	+ 1.02	+ 0.01	- 0.01
Tin and lead .. .. .	- 4.47	- 3.29	- 0.85	- 4.44 (196)
Zinc .. .. .	+ 0.77	- 1.66	+ 0.35	- 0.98

A Iodine-cetomacrogol complex. B Iodine solution. \* After 280 days or figures in parenthesis.  
a After 14 days. b After 21 days.

**Discussion**

The failure of existing iodine formulations to meet all the requirements for antibacterial applications of iodine has limited the use of this halogen. Nevertheless, the ethanol-potassium iodide solution, as weak iodine solution B.P. provides a stable formula with which to compare the iodine-cetomacrogol complex. The inclusion of an alkali iodide has been shown to increase the stability of ethanolic solutions (Courtot, 1910a; Carter, 1926). This was confirmed for storage at room temperature (14–30°), but at 37° the solution was prone to decomposition in the same manner as the simple ethanolic solution, with the production of an equivalent amount of hydrogen iodide by the oxidation of the ethanol to the corresponding aldehyde or acid (Courtot, 1910b). The decomposition of the complex also results in the production of an equivalent quantity of hydrogen iodide and hence one would similarly postulate an oxidation reaction. Table 1, however, shows that replacing the air in the ampoules with nitrogen does not decrease the amount of decomposition which occurs at room temperature. Hence, as with the production of hydrogen iodide on dissolving iodine in solutions of cetomacrogol, an oxidation reaction must be discounted, the decomposition presumably being a continuation of the "solution" phenomenon reported by Hugo & Newton (1963). The decomposition, as with the iodine solution, was not accelerated by light. Brost & Krupin (1957) recommend the inclusion of acid to prevent the decomposition and thus stabilise such complexes.

The type of the closure did not grossly affect stability but loss of solvent was more important in the case of the iodine solution than the complex.

This loss is further illustrated by reference to the storage in open beakers (Fig. 1), where approximately 50% of the solvent was lost before there was a significant loss of iodine. This loss of solvent eventually resulted in the appearance of iodine crystals and an 80% loss of iodine in 48 hr. With the complex, the final product was a dark brown water soluble paste, from which 20% of iodine had been lost in 48 hr. Of the closures tested the aluminium screw cap allowed least loss of solvent, but the aluminium was attacked by the iodine solution and the rubber liner by the iodine-ceto-macroglol complex, and therefore none of the closures was entirely suitable.

The results with more dilute solutions indicate that, under the conditions of storage, dilutions of the complex were more stable than those of the solution, in that they retained their availability and stability over a wider pH range (Fig. 2); dilutions of both systems were more stable in acid solution. The effect of water hardness on stability was probably closely linked to the presence of sodium bicarbonate rather than to the presence of other electrolytes. The pH, however, never rose above 8.0 and therefore there was no major effect on stability associated with high values of pH (Fig. 2). In the case of the iodine solution the increase in pH was sufficient to affect the stability.

The precipitation produced by the addition of potassium salts to the complex does not appear explicable by any simple theory. Van der Hoeve (1948) noted that a solution of iodine in potassium iodide produced a precipitate with polyoxyethylene ethers, and Higuchi & Guttman (1955) noted that an insoluble complex was formed between iodine in aqueous potassium iodide and polyethylene glycols. In neither case was a full explanation of the phenomenon given.

Holness & Ross (1951; 1952) and Ross (1952) have shown that non-ionic surface-active agents do not attack copper, mild steel or tin. It is assumed therefore that any corrosion by the complex is due to the presence of iodine. No attempt will be made to explain the processes involved in the attack of the various metals by the iodine systems. The results in Table 6 show that where the attack of the metals was severe, there was little difference between the two iodine systems at the 5,000  $\mu\text{g}/\text{ml}$  level. Where the attack was less, and in the case of the 100  $\mu\text{g}/\text{ml}$  solutions, the complex was generally less corrosive than the solution.

Johns (1954) reported that iodophors were non-corrosive to metals, but no details of the test procedures were given. Anderson (1957) did note that iodophors attacked aluminium, iron, copper, brass and phosphor bronze, but as the rate of corrosion did not exceed 0.1  $\text{g}/\text{m}^2/\text{hr}$  (24  $\text{mg}/\text{dm}^2/\text{day}$ ), he did not consider the attack of any practical significance. He also reported that there was no attack of stainless steel and tinplate, but again there were no details of test procedure, nor iodine concentration. If the level of practical significance of attack is taken from the work of Anderson (1957) it would be possible to classify the metals tested into those suitable and those unsuitable for use with these iodine solutions. The danger of using corrosion rates alone is shown by reference to the attack of aluminium, which could be accepted on the above rating yet marked



## IODINE-NON-IONIC SURFACE-ACTIVE AGENT COMPLEX

pitting of the samples occurred in all the solutions. Similarly, corrosion rates indicate that there is no significant attack of the tin/lead sample by the 5,000  $\mu\text{g/ml}$  iodine solution but the physical effects were clearly visible. With the low rates of corrosion which occurred in the 100  $\mu\text{g/ml}$  solution, micro- and macroscopical observations become more important. Only in the case of the stainless steel and the tin samples was there no observed effect produced on the metals. Whether or not these effects were of practical significance would depend on the conditions of practical application. It may also be noted that, in the 100  $\mu\text{g/ml}$  solutions there was a greater tendency for the sample to increase in weight, due to the formation of a film on the surface of the sample.

An additional feature was that in all cases the iodine solution needed replacing more frequently than the iodine-cetomacrogol complex. This, however, was not entirely due to the reaction with the metal, for when a control was carried out without the inclusion of a metal sample, it was found that a 100  $\mu\text{g/ml}$  dilution of the iodine solution was decolourised in 6 weeks, whereas the iodine-cetomacrogol complex of the same concentration was still yellow after 40 weeks.

From constant handling of the two preparations the general impression obtained was that the complex stained skin and fabrics to a far less extent than did the iodine solution. The attempts to verify this experimentally produced less difference than anticipated. Nevertheless, the results in Table 5 do indicate that the iodine-cetomacrogol complex was less inclined to stain, but was not completely devoid of staining properties, e.g. on woollen fabrics. This decrease in staining power could be linked with the smaller amount of iodine adsorbed from the iodine-cetomacrogol complex than the iodine solution by yeast, serum and bacteria, which has been described (Hugo & Newton, 1964).

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