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The Surface Tension of Some Oral Antiseptics

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By

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"Vere dignum et justum est, aequum et salutare, nos tibi semper, et ubique gratias agere, Domine sancte, Pater omnipotens, eaterne Deus."

Diedrich and Schaefer's
The Catholic Manual, 93, 1924

This is dedicated to my father

Franz Dziennik

Whose patience, and God fearingness are an

inspiration.

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PREFACE

The bio-chemist is now thouroughly interested in the theories and principles which underly physical Chemistry.

The results of these investigations are such, that they have brought about a change in the treatment of many diseases. It shall be the purpose of this paper to illustrate by experiment the importance of these theories and principles in oral antiseptics.

It shall be endeavoured to show that an oral antiseptic with a low surface tension is necessary for good adsorption.

That good adsorption is necessary in order to reach the bacteria that are in the deep crevices of the mouth.

The human subject was given a uniform amount of solution to wash his mouth with, for a prescribed time, at regular intervals; cultures were then taken before, and after each washing in order to determine to some degree the amount of adsorption.

Gratitudes and acknowledgments are made to all who have cooperated in whatever manner, shape, or form either in the past, or recently in this research work. Specifically to Prof.Dr. H. Heinrich, for his words of encouragement, "Everything comes to him that waits," Prof. Dr.F. C. Margoles, Prof. E. Wallner, Messrs. C. Barta, W. Kleis, and Kocowsky.

Edmund A. Dziennik

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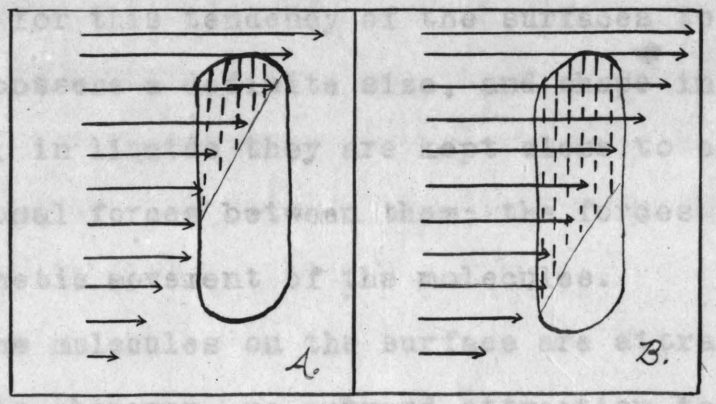
I. Theories of surface tension: adsorption; and bacterial surfaces in oral antiseptics.

The mouth of every being, man or beast, is seething with micro-organisms. Many of which are necessary and useful for such processes as mastication, digestion, respiration, and excretion of waste products. The life of the bacteria depends upon the processes mentioned, and others, because it gets its nourishment by diffusion of the various life giving substances through the cell membrane of the organism. Only in this way can the living protoplasm encased in the membrane, maintain its well being.

Diagram showing diffusion of solution through cell membrane:



(13)

A. Accelaration of a high surface tension solution. B. Of a solution with a surface tension reducent.

From the above it is seen that the oral antiseptic in order to be effective must be in solution, so that itmay readily diffuse through the cell membrane of the organism. The greater the diffusion the greater are the chances of killing the bacteria.

The surface tension of a solution is lowered by adding to it a surface tension reducent which makes it possible for a great many more molecules of the (oral antiseptic) solution

to diffuse into the cell. The theories of surface tension, adsorption, and bacterial surfaces shall be presented in the order named.

1. It is a well established fact that liquid surfaces possess the property to contract to the smallest possible area. It is evident in the spherical form of small drops of liquid.

Plateau (2) studied the forms assumed by liquid surfaces, and showed that their surfaces are always curved, and that their tendency is to contract.

It is the property of a molecule in a liquid which accounts for this tendency of the surfaces to contract. Molecules possess a definite size, and shape in all states of matter; in liquids they are kept close to each other by the cohesional forces between them; the forces do not prevent the kinetic movement of the molecules.

The molecules on the surface are attracted inwards; there is, however, no outward attraction to balance the inward attraction, because there are none outside. For this is the reason why every surface molecule is subject to a strong inward attraction, perpendicular to the surface. (3)

The well known rise of a liquid in a capillary tube is simply an automatic recording of the pressure difference across the meniscus of the liquid in the tube, the curvature of the meniscus being determined by the radius of the tube

2. The Physics and Chem. of Surfaces, N. K. Adam, 1, 1930

and the angle of contact Fig. 1 between solid and liquid.

P-a point on curve
P_1 pressure on concave side
P_2 pressure on convex side
Z- above lefel: A-below level
D_1-density on lower side
D_2-density on upper side
r-radius of tube: R-radii of meniscus:
-surface temsion

Fig. 1

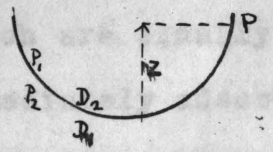
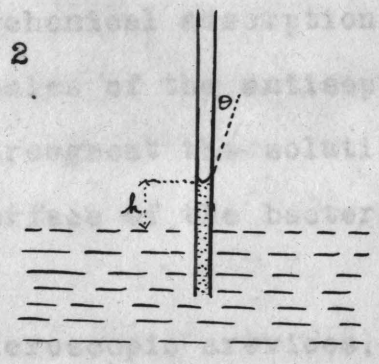


Fig. 2



Let r be the radius of the tube, θ the angle of contact between liquid and glass (generally zero). Then the radius of curvature is $\underline{r}$ and the pressure under the meniscus becomes less than that at the same height, in a liquid with a plane surface by $\frac{2 \cos \theta}{r}$. This produces a driving pressure tending to force the liquid up the tube, and the meniscus to a height, h, if D_1-D_2 is the difference between the densities of the liquid rising in the tube, and the surrounding fluid, h must be given by $\frac{2\tau \cos \theta}{r} = g\ h\ (D_1-D_2)$ or $\tau \cos \theta = 1/2\ g\ r\ h\ (D_1-D_2)$ "The liquid flows up the tube under hydrostatic pressure." Surface tension being effected by temperature, must be taken at the same temperature for accurate height readings.

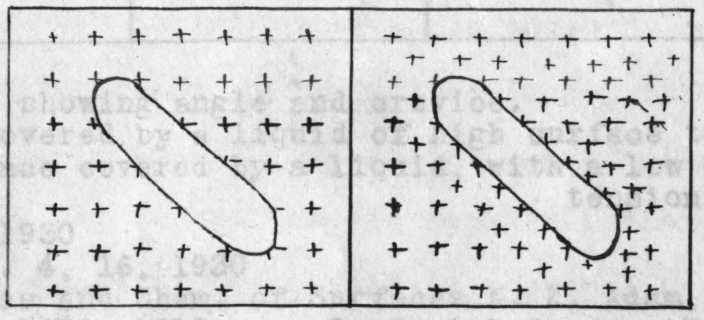
The methods and details necessary to obtain the highest accuracy by the capillary height method are more fully discussed by Richard and Coombs,[6] and Richard and Carver,[7]

and Harkins and Brown.[8]

2. Adsorption. It is a well known fact that substances which reduce the surface tension of solutions collect about any surface or particle which may be in contact with the solution, by a process of mechanical adsorption.[9] It is for this reason why the molecules of the antiseptic which are equally distributed throughout the solution, are immediately adsorbed upon the surface of the bacteria with which it might come in contact.

All tissue surfaces have microscopic crevices, fibrils, and interstices, in the depths of which there may be large numbers of organisms. The oral antiseptic must necessarily penetrate into these cavities, in order to have the surface adsorb the solution, then to diffuse still deeper into these tiny capillaries, or else any organism that remains in them, remains uninjured.

Figure 4.



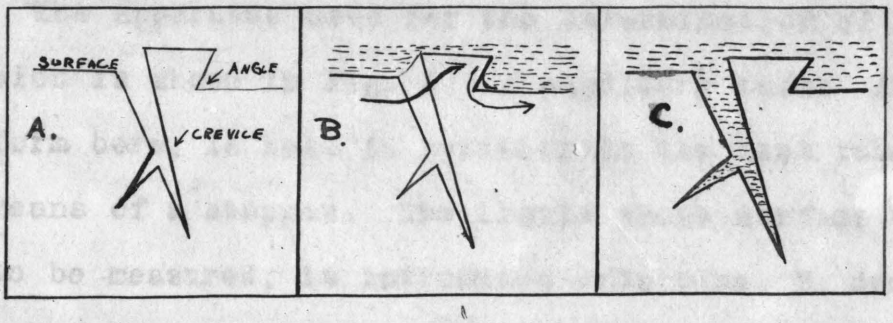
A. Adsorption of a non reducent solution by bacteria, showing equal distribution.

B. The mechanical adsorption by bacteria of solutions with lower surface tension; showing molecules on surface.

3. Bacterial surfaces; Although the surfaces of bacteria

are not strictly solid, yet the reactions which occur on them, have so much in common with reactions which occur on solid surfaces when placed in contact with an adsorbent. Charcoal will adsorb coloring matter from solution. Bacteria will adsorb coloring matter from a solution; examples can be found that hold for gases also. Quastel (10) and his colleagues, give a lengthy account of the reaction of the surfaces of Bacilli Coli in methylene blue. They(11) showed that some of the bacteria had adsorbed so much of the methylene blue, that they could not be anymore induced to start growing and proliferating again on nutrient media. This shows that a reaction took place on the surface of the bacteria.

Figure 5.



A. A surface showing angle and crevice.
B. Surface covered by a liquid of high surface tension.
C. Same surface covered by a liquid, with a low surface tension.(13)

3. Ibid 2, 1930
4. Ibid F. G. 4, 16, 1930
5 The Physics and Chem. of Surfaces N. K. Adam, 17, 1930
6. J.A.C.S. 1656, 1915
7. Ibid 827, 1921
8. Ibid 503, 1919
9. Dental Cosmos, W.A. Feirer, Sept., 1927
(10)Bio-Chem. J. Quastel20, 166, 1926
(11) Ibid Quastel and Woodbridge, 21, 1224. 1927

II Oral antiseptics investigated.

The following oral antiseptics were investigated: Antiseptic Solution N. F., Glyco Thymoline, Hexyl Resorcinol, Hydrogen Peroxide, Lavoris, Listerine, Pepsodent, and Zonite.

These substances were used because they are extensively used, and are nationally known.

The capillary rise method was employed to determine the surface tension of these various antiseptics. For the experimental details of this method, Richards, Carver, Hunten and Mass may be consulted.(12) According to their experiments and opinion, the percentage of error is the least in the capillary rise method.

The apparatus used for the determination of surface tension is shown in Fig. 6. A capillary tube: A, of uniform bore, is held in position in the test tube, B, by means of a stopper. The liquid whose surface tension is to be measured, is introduced into tube, B, cork inserted, and tube placed inside of the larger tube, C. Water is placed in tube, C, which is placed in another water bath, D, the temperature is kept constant, the capillary elevation of the liquid is measured by a centimeter scale, E, back of tube, A. The vents in both stoppers permit the excape of vapor from the liquid in, B, and C, insuring equal pressure inside and outside

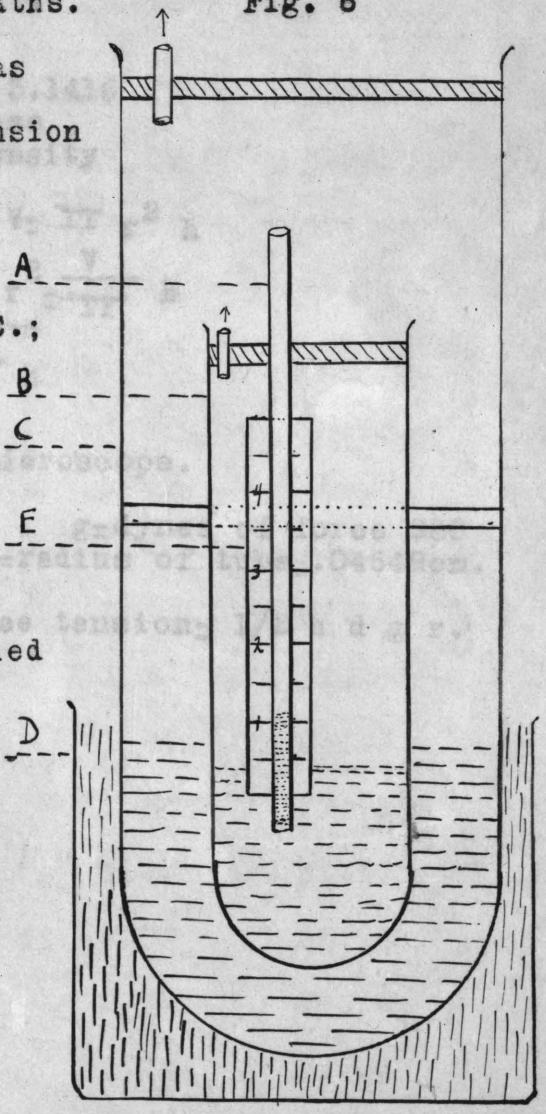
12. J. A. C. S. 156--1929
13. Journal Infectuous Diseases, M. Frobisher, 66,38,1926

the apparatus. The surface tension of a liquid has been found to depend upon the nature of the liquid, and upon the temperature. For this reason the bath must be kept at a constant temperature. The following concentrations were used:

1. Full strength
2. 20% "
3. 4% "
4. 2% "

The concentrations were selected because they are recommended by the manufacturers of the preparations. Different concentrations are necessary for open cuts, and wounds mouth washes, and eye baths.

Fig. 6



The following technique was followed in all the surface tension determinations:

1. The water bath was kept at a constant temperature, 20°C.;

2. The pycnometers used for density determinations were always washed in an acid cleaning solution, rinsed well with water, placed in oven, dried in dessicator, cooled, used again.

3. The capillary tube was washed in an acid solution, rinsed with water and alcohol, placed in oven, dried, cooled, used again.

Free from foreign substances such as aromatic oils.

4. The following formula was used:

d=density
h=height in cm.
g=dynes force
r=radius of tube
γ =surface tension

$\frac{2\gamma \cos.\theta}{r} = g\ h\ d$ or

$\gamma \cos\theta = 1/2\ g\ h\ d\ r$: Since cos.$\theta$ is so small, it shall be considered as cos. θ=0.

$$\gamma = \frac{g\ h\ d\ r}{2\ \cos.\theta}$$

$$\gamma = 1/2\ g\ h\ d\ r$$

Since the diameter of the tube was unkown, it was found by formula; by filling the tube with mercury; and its volume determined. The radius was then calculated.

h=length of tube
r=radius
V=volume

π= 3.1416
M=Mass
D=density

$$D = \frac{M}{V} \qquad V = \pi r^2 h$$

$$V = \frac{M}{D} \qquad r^2 = \frac{V}{\pi h}$$

$$r = \sqrt{\frac{V}{\pi h}}$$

It was also measured with the microscope.

h=capillary rise in cm.
d=density of solution= $\frac{wt.}{vol.}$
g=dynes of force 980
r=radius of tube=.04649cm.

Surface tension= 1/2 h d g r.

Table I

Surface Tension of: Antiseptic Sol. N. F., Glyco Thymoline; Hexyl Resorcinol; Hydrogen Peroxide; Lavoris; Listerine; Pepsodent, and Zonite, at 20° C.; Radius of tube .04649 cm.

(D) Density: (H) Height in Cm.: (S.T.) Surface Tension in dynes. (F.S.) Full strength:

Substance	Concentration	D.	H.	S.T.
Antiseptic Solution	F.S.	.980	1.45	32.37
"	20%	.950	1.73	39.21
"	4%	.989	1.76	39.65
"	2%	.999	1.8	40.96
Glyco Thymol.	F.S	1.06	1.65	39.84
"	20%	1.01	1.40	32.21
"	4%	1.00	1.49	33.94
"	2%	1.01	1.09	25.08
Hexyl Resorc.	F.S.	1.08	1.30	31.99
"	20%	1.01	1.72	39.58
"	4%	1.00	2.3	52.39
"	2%	1.00	1.47	33.48
Hydrogen Perox.	F.S.	1.01.	1.64	37.73
"	20%	1.00	1.43	32.57
"	4%	1.00	1.57	35.76
"	2%	1.00	1.71	38.96
Lavoris	F.S.	.998	1.74	39.56

Substance	Concentration	D.	H.	S. T.
Lavoris	20%	.999	1.2	27.31
"	4%	.998	1.81	41.15
"	2%	.989	2.05	46.19
Listerine	F.S.	.966	1.50	32.26
"	20%	.995	1.65	37.4
"	4%	.998	1.60	36.38
"	2%	1.00	1.54	35.08
Pepsodent	F.S	.998	1.45	31.94
"	20%	.999	1.8	40.97
"	4%	.999	2.10	48.90
"	2%	1.09	1.86	45.45
Zonite	F.S	1.1	1.78	44.6
"	20%	1.02	2.40	55.77
"	4%	1.01	2.60	59.82

B. For determining the adsorptioned value of an oral antiseptic as a mouth wash it was necessary to have human subjects. The subjects were told the purpose of the experiment. Consent was given on condition that the names of the bacteria, and the bacterial count would not be mentioned. Therefore names of the bacteria found and their counts shall not be given because of the trust. Comparative adjectives shall be used instead, as an indication of the effectiveness:

Procedure: 1. 80 cc of a 1 to 3 solution was made of all the antiseptics; good for four mouth washings, of

20 cc each.

2. A culture was taken from each subjects mouth with a sterile applicator, before each washing.

3. The culture was placed on an agar media, placed in an incubator, and incubated for 48 hours.

4. The growth was determined at the end of 48 hours.

5. The oral antiseptic was held in the mouth for two minutes, then ejected.

6. The mouth was washed hourly.

7. Fasting was observed during the entire four hours.

A day elapsed before group B, of the antiseptics could be tested. It was impossible to have the subjects present on the following day, and also because some of the solutions irritated the subjects gums.

Technique.

The applicators were sterilized in gas heated oven for an hour, and sealed in sterile envelopes.
The agar media, was made by dissolving 31 gm. of Agar in 1 liter of hot distilled water. Then poured into 6 inch test tubes. The tubes were then placed into an autoclave steam sterilizer, at 130° C. and 25 lbs. pressure. The test tubes were sealed by a cotton wad, and sterilized by holding it over an open flame. The incubator was electrically heated, and regualted, for 33° C. U.S. Dept. of Public Health, technique was followed in general.

Table II

(Sub.)Subject; (Con.)Concentration; (A.S.)Amount of solution in cc.; (T.S.)Time solution held in mouth in minutes; (Cul.)Culture No. 1 hr. interval; (Grow.)Growth; (Eff.)Effectiveness.

Sub.	Substance	Con.	A.S.	T.S.	Cul.	Grow.	Eff.
A					P1	+	Control
"	Pepsodent	25%	20	2	P2	+	Not noticeable
"	"	"	"	"	P3	+	Fewer
"	"	"	"	"	P4	+	Less
"	"	"	"	"	P5	+	Least
B					H1	+	Control
"	Hexyl Resorcinol	25%	20	2	H2	+	Slightly reduced
"	"	"	"	"	H3	+	Same
"	"	"	"	"	H4	+	Greatly reduced
"	"	"	"	"	H5	+	Fewer
C					Z1	+	Control
"	Zonite	25%	20	2	Z2	+	Few
"	"	"	"	"	Z3	+	Least
"	"	"	"	"	Z4	+	Same
"	"	"	"	"	Z5	+	Fewest
D					L1	+	Control
"	Listerine	25%	20	2	L2	+	Same
"	"	"	"	"	L3	+	Fewer
"	"	"	"	"	L4	+	Fewer
"	"	"	"	"	L5	+	Same

Group B.

Sub.	Substance	Con.	A.S.	T.S,	Cul.	Grow.	Eff.
A					G1	+	Control
"	Glyco Thymo-line	25%	20	2	G2	+	Same
"	"	"	"	"	G3	+	Fewer
"	"	"	"	"	G4	+	Same
"	"	"	"	"	G5	+	Slightly reduced
B					R1	+	Control
"	Lavoris	25%	20	2	R2	+	Same
"	"	"	"	"	R3	+	Fewer
"	"	"	"	"	R4	+	Less
"	"	"	"	"	R5	+	Same
C					A1	+	Control
"	Antiseptic Sol.	25%	20	2	A2	+	Same
"	"	"	"	"	A3	+	Fewer
"	"	"	"	"	A4	+	Same
"	"	"	"	"	A5	+	Less
C	Hydrogen Per-oxide				O1	+	Slightly
"	"	25%	20	2	O2	+	Fewer
"	"	"	"	"	O3	+	in
"	"	"	"	"	O4	+	each
"	"	"	"	"	O5	+	culture

+ Means that bacteria were present.

Cultures H5 and P5 show the least amount of bacteria over the control. Cultures A2 and A5 show a reduction

over the control. In general all cultures show a reduction over the control.

Cultures of series P, H, and Z, showed the least bacteria growths. The bacteria present in some control cultures had entirely disappeared in the later ones, showing by experiment the germicidal and adsorptive effectiveness of the solutions.

C. The combined results show that an oral antiseptic must not only have a low surface tension, but that it must also have a high germicidal coefficient.

Hydrogen Peroxide for instance has a much lower surface tension and a much lower germicidal coefficient than Zonite.

Lavoris and Pepsodent have a surface tension nearly alike. Therefore both must have penetrated to the same depths. Allowing the rate of diffusion and of adsorption to be the same for each; it would be expected to get the same germicidal coefficient, which however, was not the case, as each was different. Assuming the bacteria withstood the chemical reaciton within its protoplasm of the former but not of the latter. Or possibly there was a chemical reaction between the organic matter in the mouth, and the antiseptic. This proves that the chemical or chemicals in Pepsodent are more injurious to bacteria, and more stable, than those of Lavoris. If not the bacteria would have survived and kept on multiplying as in Lavoris.

However, it is not entirely fair to make this comparison as a different subject is involved with each oral antiseptic. The physical development of the bacteria could have been different in each case even if they were the same type.

The following antiseptics were used in the order named, by the same subject on alternating days: Zonite, Antiseptic Sol. N. F., and Hydrogen Peroxide, therefore it is a better comparison. The second and third have lower surface tensions than the first, the third is lowest. As germicides they rank in the following order: Zonite, first; Hydrogen Peroxide, second; and Antiseptic Sol. N. F.; third; again proving that the constituent chemicals in the antiseptic constitute an important part in the oral antiseptic. And that surface tension and diffusion of the antiseptic into bacteria alone will not kill the bacteria, it must be the chemical that sets up an injurious reaction to the bacterias' protoplasm, that decides the germicidal effectiveness of an oral antiseptic to a large extent.

Pepsodent and Hexyl Resorcinol showed that they have within their solution the combined requisites, low surface tension, high adsorption, chemical stability, and high germicidal properties. The former is an alcoholic solution which would imply that the chemical constituent is not a surface tension reducent; but that the alcohol is added as a surface tension reducent. The latter is

an equeous solution which implies that the chemical constituent itself is a surface tension reducent and a strong germicide. All the solutions are alcoholic except the following: Hydrogen Peroxide, Hexyl Resorcinol, and Zonite.

D. Getting uniform capillary rise was experienced with some of the solutions, with an oil and alcohol content, which may have been due to ionization, or some other molecular, or physical reaction. The reading of the plane surface and meniscus was also difficult at times, and in order to have greater accuracy, the apparatus would have to be improved for this difficulty.

There is still much to be investigated in the adsorption theory. Why is it that some bacteria can withstand one germicide and not another, even if the surface tension is low? Why some germicides can kill the bacteria in a weak solution and not in a highly concentrated solution?

In order to get good adsorption, it is the writers' belief that it might be useful to saponify the organic substances in the mouth. This would leave the surface clean and more free of organic matter. The antiseptic would then not be reacted upon to the same degree by the remaining organic substances, and the germicidal effectiveness would increase accordingly, as it would penetrate deeper, and would be adsorbed more.

There are many phases of this problem to be inves-

tigated. Research must be carried on until a solution or substance is found that will overcome all or most of these obstacles. The problem is large, and important because it involves living matter, and the well being of man. It has been proven by experiment that a good oral antiseptic in order to be effective should have these and other properties: 1. A low surface tension. 2. High penetrating power. 3. High adsorptive power. 4. High germicidal power.

The best way to keep down the bacterial content of the mouth would be by brushing the teeth and gums regularly and using a good oral antiseptic after it; so as to disinfect the surface, of the mucuous membrane.

Deo Gratia.

Bibliography

(1) Diedrich and Schaefer's The Catholic Manual,93,1924.

(2)The Physics and Chemistry of Surfaces,N.K.Adams,1930.

(3) Ibid.2,1930.

(4) Ibid,16,1930.

(5) Ibid,17,1930/.

(6) Journal American Chemical Society,1656,1915.

(7)Ibid,827,1921.

(8) Ibid,503,1919.

(9) Dental Cosmos,W.A.Feirer,Sept.1927.

(10) Bio-Chem.Journal,Quastel,20,166,1926.

(11) Ibid.Quastel and Woodbridge,21,1224,1927.

(12) J.A.C.S. 156,1929.

(13) Journal Infectuous Diseases,M.Frobisher,66,38,1926.