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The Use of Surface Active Agents to Prevent 'Precipitate Crawling' and to Speed Filtration in Gravimetric Determinations

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The purpose of this investigation was to determine the relationship, if any, between a reduction in surface tension and the phenomenon known as 'precipitate crawling'. In order to accomplish this, various surface active agents were introduced into the procedure for the determination of nickel as nickel-dimethylglyoxime. This precipitate was chosen because it was known to exhibit the phenomenon of 'crawling' to a marked extent. This tendency to 'crawl' increases the chance for inaccurate results in quantitative determinations by making it difficult and time-consuming to effect the transfer of precipitate from beaker to Gooch.

The problem was twofold: to determine first if 'crawling' could be decreased by a reduction in surface tension; and second, if the precipitation remains quantitative when surface active agents are used.

In order to detect any decrease in 'crawling' it was necessary to use almost completely visual means since no suitable quantitative measurement of this phenomenon is possible. However, the use of these agents would be warranted only if the decrease in 'crawling' was great enough to be plainly visible to the eye.

The effect these agents might have on the accuracy of the determination could be detected by analyzing steel samples of known nickel content and comparing the results with the known value and with 'control' determinations, *i. e.*, determinations using no surface active agents. If the accuracy of the determination is affected by these agents, their use would not be warranted regardless of how effective they might be in preventing 'crawling'.

CLASSIFICATION OF DETERGENTS

A glance at the following classification of surface active agents by McCutcheon [1] will give some idea of the types of agents that may be chosen.

I Alcohol sulfates
II Alkyl-aryl sulfonates
III Alkyl sulfonates
IV Sulfated or sulfonated amides
V » » » esters
VI » » » amines
VII Miscellaneous types
VIII Cationic agents

From these groups it was possible to obtain cationic, anionic or neutral agents that were stable over a wide range of pH and toward most oxidizing and reducing agents.

SUREACE TENSION REDUCTION

The first question that arose was how much agent to use. In order to answer this a surface tension analysis was run testing various agents on a 'blank' solution, that is, a solution identical in all respects to an actual determination except that no steel sample was used. The results of this analysis gave the most effective concentration of surface active agent with respect to an approximately maximum decrease in surface tension.

Table 1. Liquid agents.

Amount per 50 ml 'blank' sol.	Igepal	Santo-merse	Triton 770	Sterox SK	Triton X-155	Triton 720	Triton N-100
	γ	γ	γ	γ	γ	γ	γ
0 drops **	55.56	55.56	55.56	55.56	55.56	55.56	55.56
1 drop	39.64	31.68	54.28	42.6	44.8	32.68	34.38
2 drops	32.30 *	30.55 *	40.35	31.2 *	42.6	31.26 *	33.11
3 drops	32.30	31.36	35.52	34.1	35.8	31.26	31.83 *
4 drops	33.11	—	31.12 *	—	32.1 *	—	32.68
5 drops	—	—	32.11	—	32.7	—	—

* Most effective concentration.

** Concentration of commercial product.

Table 2. Solid agents.

Amount per 50 ml 'blank' solution	Vel	Nacconol NRSF
	γ	γ
.00 g	55.56	55.56
.05 g	35.09	38.08
.10 g	30.69	31.40
.15 g	30.26 *	29.27 *
.20 g	30.69	30.98

* Most effective concentration.

Tables 1 and 2 show the results of the analysis for the nine agents used in the quantitative determinations. Surface tension (γ) is expressed in dynes per centimeter.

QUANTITATIVE RESULTS

The effectiveness of the different agents is illustrated by Figs. 1 and 2.

Two quantitative tests were run with each surface active agent using the standard procedure as outlined by Kolthoff and Sandell [2]. Samples A

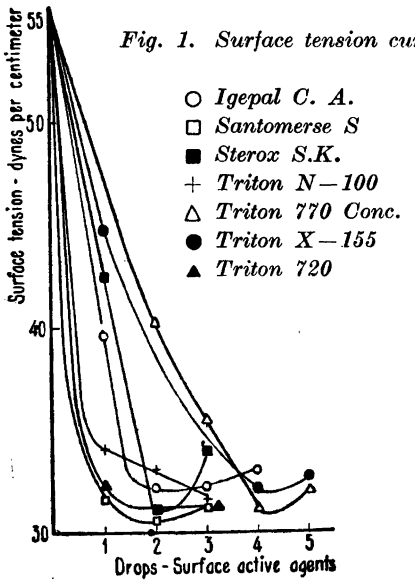

Fig. 1. Surface tension curves.

○ *Igepal C. A.*
□ *Santomerse S*
■ *Sterox S.K.*
\+ *Triton N—100*
△ *Triton 770 Conc.*
● *Triton X—155*
▲ *Triton 720*

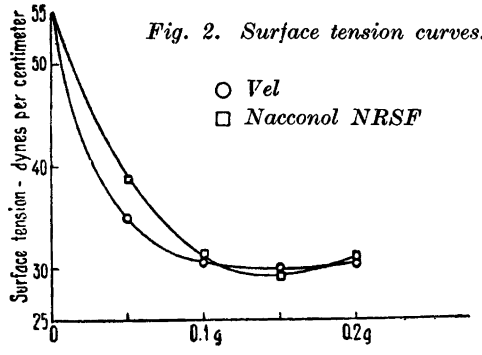

Fig. 2. Surface tension curves.

○ *Vel*
□ *Nacconol NRSF*

had the agent added to the cold acid solution before the addition of dimethylglyoxime, while Samples B had it added to the hot basic solution after precipitation. The only other change from the standard procedure was that the solutions were filtered by decantation and washed twice with a water solution of the same surface active agent used in the determination. The transfer of precipitate was accomplished by using this surface active wash liquid and was so effective that no rubber policeman was required. While in the Gooch, the precipitate was washed twice with hot pure water.

The effectiveness of this method in removing all foreign matter and all excess surface active agent was tested by shaking a water solution of a dried and washed precipitate and a dried but unwashed one in individual test tubes.

Table 3. Quantitative results.

Agent used	Sample	Wt. of sample	Wt. of dimethylglyoxime ppt.	Percent (computed)	Percent (actual)	Error
Control	1	1.6785 g	0.0317 g	0.5973	0.61 *	− 0.013
»	2	1.3649	0.0426	0.6342	0.61	+ 0.024
»	3	1.0847	0.0355	0.6647	0.63 **	+ 0.035
»	4	1.0611	0.0340	0.6507	0.63	+ 0.021
Igepal C. A.	A	1.0766	0.0326	0.6154	0.61	+ 0.005
	B	1.0071	0.0317	0.6395	0.61	+ 0.029
Vel	A	1.1787	0.0364	0.6361	0.61	+ 0.026
	B	0.8992	0.0280	0.6328	0.61	+ 0.023
Triton N-100	A	1.0256	0.0345	0.6835	0.61	+ 0.074
	B	1.0275	0.0338	0.6684	0.61	+ 0.058
Santomerse S	A	1.0460	0.0054	0.1049	0.61	− 0.505
	B	1.0974	0.0175	0.3240	0.61	− 0.286
Triton 770	A	1.0387	0.0323	0.6319	0.61	+ 0.022
	B	Discarded — Filtration unsatisfactory				
Sterox SK	A	1.1106	0.0310	0.5672	0.61	− 0.043
	B	1.0270	0.0315	0.6232	0.61	+ 0.013
Triton X-155	A	Discarded — Filtration unsatisfactory				
	B	1.0389	0.0334	0.6533	0.63	+ 0.023
Triton 720	A	1.1080	0.0371	0.6804	0.63	+ 0.050
	B	1.0168	0.0339	0.6774	0.63	+ 0.047
Nacconol NRSF	A	1.0003	0.0306	0.6216	0.63	− 0.008
	B	1.0419	0.0325	0.6338	0.63	+ 0.004

* Analyzed sample obtained from Smith and Underwood, sample no. 12.

** Analyzed sample obtained from Smith and Underwood, sample no. 14.

The washed and dried precipitate showed no foaming tendency, whereas the other foamed considerably.

The results of these determinations were then compared with four »control» determinations as to 'crawling', ease of precipitate transfer, speed of filtration, and accuracy. The quantitative results were also compared with the percent nickel known to be present in the sample.

Table 3 shows the quantitative results of these determinations.

EFFECT ON 'CRAWLING'

The conclusion from this investigation was that one of the main causes of 'crawling' as exhibited by nickel-dimethylglyoxime is surface tension, since its reduction by use of surface active agents removes all observable tendencies of the precipitate to 'crawl'.

Figures 3 to 6 show the difference in 'crawling' tendencies of the precipitate in a 'control' and a 'surface active' solution. It will be noticed that the 'control' precipitate 'crawls' considerably both in the beaker and in the Gooch, whereas the 'surface active' precipitate shows no tendency to 'crawl'.

This conclusion would naturally lead one to question whether the use of surface active agents is applicable to other determinations in which the precipitate exhibits this phenomenon. Mr. G. Chen, of Drew University, used Igepal C. A. in connection with the determination of nickel in nickel ore and found that all 'crawling' tendencies were removed, filtration and washing time was reduced by one-third, and the accuracy was within $\pm$ 0.03 %. These results tended to confirm the results of the author even in a substance of considerably higher nickel content.

Qualitative tests were run testing the effectiveness of various agents on the 'crawling' tendencies of the ammonium phosphomolybdate precipitate. It was found that some agents, such as Igepal C. A., either had no effect on 'crawling' or even increased it; some, such as Santomerse S and Nacconol NRSF, removed 'crawling' tendencies; some, such as Sterox S. K., caused the formation of a gum-like precipitate; and some, such as Vel, reacted themselves with the molybdate reagent to form insoluble precipitates.

It would appear that certain surface active agents could be found that would remove 'crawling' and facilitate the transfer or removal of almost any precipitate that exhibits this phenomenon.

QUANTITATIVENESS

The use of surface active agents, except for Santomerse S, apparently does not interfere with the quantitativeness of the determination of nickel.

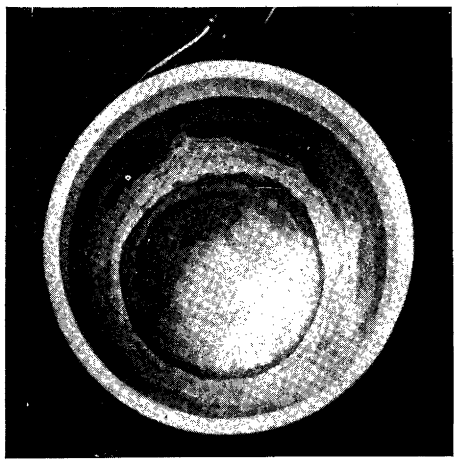

Fig. 3. Gooch crucible after filtration — no surface-active agent used.

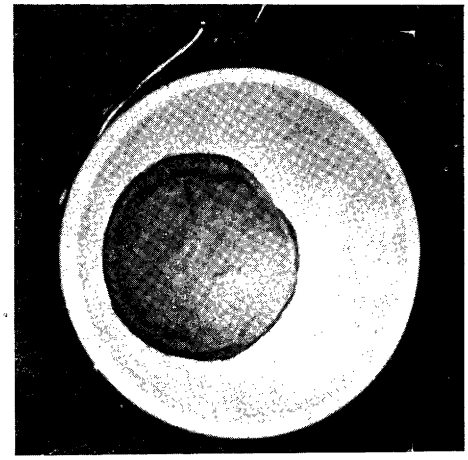

Fig. 4. Gooch crucible after filtration — surface-active agent added.

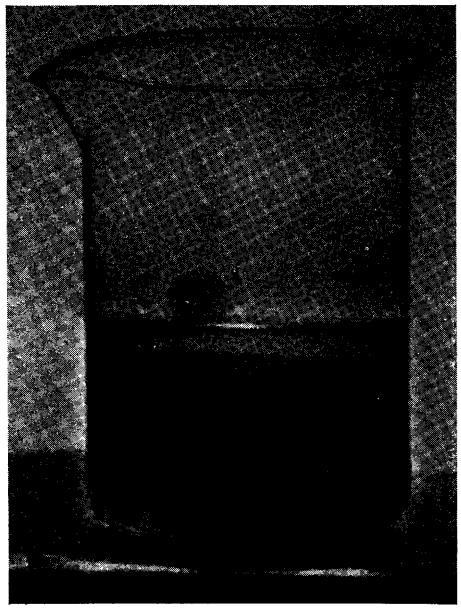

Fig. 5. Precipitate 'crawling' in 'control' solution.

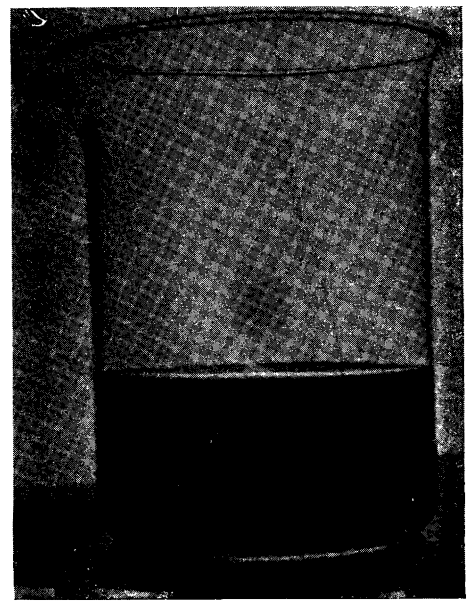

Fig. 6. Absence of 'crawling' in surface-active solution.

In a determination of this sort an error of ± 0.1 % is generally considered to be the maximum which may be conceeded to inherent errors in the determination and personal errors. It will be noticed that, except for the very low results of Santomerse S, the range of error is from 0 to ± 0.07 %, which is well within the allowable limit. This range also compares favorably with the 0 to ± 0.04 % error obtained from the 'control' solutions.

The effect of Santomerse S on the precipitate is not known with certainty. However, a microscopic analysis of the residue after drying showed that very few of the characteristic crystals of nickel-dimethylglyoxime were present. The main bulk of the precipitate was a dark brown amorphous solid. This observation would lead one to believe that Santomerse S either forms a complex ion with nickel and thereby prevents complete precepitation, peptizes the precipitate, or forms a precipitate itself with nickel.

FILTRATION SPEED

An attempt was made to prepare all Gooches with mats of approximately similar thickness and density in order to permit a comparison of the filtration times of the various solutions. Obviously this was practically impossible to accomplish and variations of 10 to 15 minutes in filtration time might very easily be due to variations in the respective mats. This might tend to explain the difference of 19 to 37 minutes filtration time for the »control» solutions; but it would not, in itself, be sufficient to explain the variation of 6 minutes to over 2 hours for the 'Surface active' solutions. Apparently the agents affect the precipitate in some way that causes a great difference in its ability to be filtered. The exact mechanism by which this is effected could not be determined. It is believed, however, that the agglomeration tendencies of the precipitate are varied by the use of surface active agents and this, in turn, affects the speed of filtration.

Whether the variation between the more efficient surface active solutions and the 'control' solutions is due to some change in the properties of the precipitate or only to the increased ease of precipitate transfer is not known. The fact remains, however, that certain surface active agents not only remove 'crawling' tendencies but also increase, to some extent, the speed of filtration.

MICROSCOPIC ANALYSIS

The precipitates from Igepal CA, Sterox SK, Triton 770, and 'control' solutions were examined by means of a microscope equipped with a micrometer eyepiece. The characteristic red monoclinic crystals of nickel-dimethyl-

glyoxime of approximately 25 μ length and 1 μ diameter were apparent in all four cases.

The agglomeration tendencies, however, did seem to vary since in the 'control' and Triton 770 solutions the precipitates seemed to consist of individual crystals, whereas the others were aggregates.

The precipitate from the Santomerse S solution was found to consist mainly of a dark brown amorphous solid with very little nickel-dimethylglyoxime present.

Table 4. Summary.

Surface active agent	Classification (type)	Sample	Deviation from accepted percent nickel	Observed 'crawling' tendencies	Filtration and washing time	Ease of transfer of ppt.
None (Control)	—	1	− 0.013	Bad	31 min	Very poor
» »	—	2	+ 0.024	»	37 »	» »
» »	—	3	+ 0.035	»	20 »	Poor
» »	—	4	+ 0.021	»	19 »	»
Santomerse S	II	A	− 0.505	None	20 »	Excellent
» »	»	B	− 0.286	»	7 »	»
Nacconol NRSF	»	A	− 0.008	»	1 h	»
» »	»	B	+ 0.004	»	6 min	»
Vel	V	A	+ 0.026	»	14 »	»
»	»	B	+ 0.023	»	2 h	Very good
Igepal C. A.	VII	A	+ 0.005	»	12 min	Excellent
» »	»	B	+ 0.029	»	16 »	»
Triton X-155	»	A	—	»	Filtration stopped	—
» »	»	B	+ 0.023	»	22 min	Excellent
Triton N-100	»	A	+ 0.074	»	9 »	»
» »	»	B	+ 0.058	»	11 »	»
Triton 770	»	A	+ 0.022	»	1 + h	»
» 770	»	B	—	»	Filtration Stopped	—
Sterox SK	»	A	− 0.043	»	10 min	Excellent
» »	»	B	+ 0.013	»	9 »	»
Triton 720	»	A	+ 0.050	»	26 »	»
» 720	»	B	+ 0.047	»	17 »	»

SUMMARY

Table 4 summarizes the results of the investigation and shows that certain surface active agents are capable of preventing 'crawling', speeding filtration, and maintaining accuracy in the determination of nickel as nickel-dimethylglyoxime. The agents are classified according to the types given by McCutcheon, listed earlier in this article. Some manufacturers are reluctant to furnish detailed information as to the types to which their products belong.

REFERENCES

1. McCutcheon, J. W. *Chem. Ind.* **61** (1947) 5, 812.
2. Kolthoff, I. M., and Sandell, E. B. *Textbook of quantitative inorganic analysis N. Y. C.* (1947) 722.

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