The Electrolytic Preparation of Vanadium(II) Developers

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Since photographic development is essentially the reduction of silver ions, the ability of a developing agent can be estimated by the degree of its reducing power, by, that is, the redox potential. According to Reinders,[1] when the redox potential of a developer is more negative than +0.120 V. with respect to the standard hydrogen electrode, a silver bromide particle containing a latent image can be reduced.

Vanadium can take the ionic state in the aqueous solution from +5 to +2 valencies, among which range the vanadous ion (V^{2+}) shows a strong reducing power and the redox potential of the system V^{2+}-V^{3+} is:

$$E^\circ = -0.25_5 \text{ V. } (25^\circ\text{C})^{2)}$$

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[1] W. Reinders, *J. Phys. Chem.*, **38**, 783 (1934); *Sci. Ind. Phot.*, **5**, 284 (1934); **6**, 297 (1935).

[2] G. Jones and J. Colvin, *J. Am. Chem. Soc.*, **66**, 1573 (1944).

This value seems suitable for photographic development. Further, in order for such a polyvalent ion to be suitable for the development, both the reductant (V^{2+}) and the oxidant (V^{3+}) before and after the development should be soluble in water, and vanadous ion satisfies this requirement also. The developing reaction may be shown in the following equation:

$$Ag^{+}+V^{2+} \rightarrow Ag+V^{3+}$$

Lumiére[3] reported the first use of vanadium salt as a developing agent at the end of the 19th century. After that, no studies were reported on it until 1952 when Roman[4] carried out the fundamental studies for a rapid developing process using V^{2+} salt. Rasch and Crabtree and their co-workers[5-7] also studied this process and especially its application to the development of motion picture positive films, while Fortmiller and James[8] discussed the rate process of this development. In Japan, this process was taken up by the Institute of Industrial Science of the University of Tokyo and by the NHK Technical Research Laboratories. The former constructed a developing machine for reversal and positive films,[9] and the latter gained experience in developing positive films for television use.[10] The processing using the vanadium developer was summarized by Kikuchi.[11]

The characteristics of the vanadium developer are very superior according to the above-mentioned studies, but in actual automatic processing, it is difficult to obtain a good reproducibility due to the different composition of the developer solution, the contamination of the developer, and the unstability of the vanadous ion. It is, therefore, important to prepare a developing solution of a fixed composition. The vanadium developer can also be regenerated electrolytically during development by circulating the solution, so it is necessary to establish the electrolytic conditions. From these standpoints, the preparation of the vanadium developer, including the electrolytic process, will be studied in detail in the present paper.

As the vanadium pentoxide (V_2O_5) is the most easily available commercially-produced vanadium compound, it is adopted as the starting material. A method for obtaining the vanadous ion electrolytically from metallic vanadium has been reported,[12] but it seems to the author not to be practical. Although ammonium metavanadate is also available, it is not used in the present study.

In starting with vanadium pentoxide, it is necessary to reduce V^{5+} to the V^{2+} state. This reduction process consists of the following two steps:

$V^{5+} \rightarrow V^{4+}$, chemical reduction process

$V^{4+} \rightarrow V^{3+} \rightarrow V^{2+}$, electrolytic reduction process

The present paper is, therefore, divided into two parts.

Chemical Reduction Process

As has been mentioned above, this process is the reduction from V^{5+} to V^{4+}, but V^{4+} usually exists in the form of VO^{2+} salt (vanadyl salt) in an aqueous solution. Accordingly, this process is a preparation of vanadyl salt. Three methods are known for preparing vanadyl salt from vanadium pentoxide, (i) the sulfur dioxide process, (ii) the hydrobromic acid process, and (iii) the oxalic acid process.

The preliminary experiences with these three processes have shown that all of them gave a good yield of vanadyl salt, but in process i, excess sulfur dioxide remained in the reaction solution, which was apt to form hydrogen sulfide during the succeeding process of electrolytic reduction and so cause fog. In process ii, the evolution of bromine during the reaction led to considerable difficulty in manipulation. Finally, process iii was adopted as the best one to obtain the pure vanadyl salt. Another advantage of process iii is that the vanadyl ion can be obtained coupled with an optional anion, depending upon the kind of acid used. For example, when sulfuric acid is used, vanadyl sulfate ($VOSO_4$) is obtained, while in case of the hydrochloric acid, vanadyl chloride ($VOCl_2$) is formed. In this study, the syntheses of vanadyl sulfate, vanadyl chloride and vanadyl nitrate are examined.

Experimental

Material. — The vanadium pentoxide used is yellowish-brown, amorphous and of an extra-pure grade. Extra-pure-grade oxalic acid dihydrate and sulfuric acid, hydrochloric acid and nitric acid of various concentrations are used.

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3) A. and L. Lumiére, *Bull. Soc. Fr. Phot.*, **10**, 108 (1894).

4) P. Roman, *Sci. Ind. Phot.*, **23**, 417 (1952).

5) C. Ives, H. Russell and J. Crabtree, *J. Phot. Sci.*, **2**, 7 (1954).

6) A. Rasch and J. Crabtree, PSA technical quarterly, May, 59 (1954).

7) A. Rasch and J. Crabtree, *J.S.M.P.T.E.*, **62**, 1 (1954).

8) L. Fortmiller and T. James, Roy. Phot. Soc. Centenary Conference, Sept., 161 (1953).

9) S. Kikuchi, C. Yoshinaga, W. Fujita, K. Tanimura and K. Akaike, *J. Soc. Sci. Phot. Japan*, **19**, 40 (1956).

10) T. Kitagawa, K. Akaike and K. Hiwatari, ibid., **20**, 62 (1957).

11) S. Kikuchi, *Denki-kagaku*, **24**, 59 (1956).

12) J. Brierley, *J. Chem. Soc.*, **49**, 822 (1886); A. Piccini, *Z. anorg. Chem.*, **19**, 204 (1899); A. Piccini and L. Marino ibid., 32, 55, 71 (1902).

Procedure. — A calculated weight of vanadium pentoxide is added to the sulfuric acid. As vanadium pentoxide is not easily soluble in sulfuric acid, most of it is suspended as a brownish color. When vigorously stirred, the oxalic acid dihydrate is added slowly into the solution while it is being heated. The reducing reaction proceeds during a vigorous evolution of carbon dioxide. When the added oxalic acid is completely consumed, the evolution of gas stops and the addition of oxalic acid is again continued. As the reaction proceeds, the solution becomes blue-green, the reaction is considered to be over when the yellowish-brown particles of vanadium pentoxide completely disappear.

Results

The Synthesis of Vanadyl Sulfate. — The vanadyl sulfate solution can be directly used for electrolysis, but in order to use the pure vanadyl sulfate for it and to ascertain the yield of this process, the vanadyl sulfate was isolated. The reaction solution was filtered to remove the unreacted vanadium pentoxide and condensed on a water bath. When the solution was left to cool for about 24 hr., blue crystals of vanadyl sulfate, which were somewhat hygroscopic, were obtained. From the weight of crystals, a crude yield is given.

As this crystal is considered to contain sulfuric acid and water, further purification was carried out. This was achieved by means of repeated washing in ethanol and water, utilizing the good solubility of sulfuric acid in water and the difference in the solubility of vanadyl sulfate between that in water and that in ethanol (it is more easily soluble in water). The crystals were then filtered and dried to obtain pale blue, powdery crystals. From the weight of the crystals thus obtained, the yield of purification is given. The loss caused by purification sometimes reaches a 40% maximum. The purified crystals were considered to have the constitution of $VOSO_4 \cdot xH_2O$, so the VO^{2+} ion content in the crystal was determined in order to decide x by means of oxidation titration with ceric sulfate. The results showed the content of 31%. Hence, x is equal to 3. In other words, it is clear that vanadyl sulfate crystal contains 3 molecules of the water of crystallization. This crystal is not hygroscopic and is sufficiently stable in the open air. The final results are shown in Table I.

TABLE I. SYNTHETIC CONDITIONS OF VANADYL SULFATE

Material			No. 1	No. 2	No. 3
V_2O_5,	g.		10	40	50
H_2SO_4 (95%),	ml.		20	40	50
H_2O,	ml.		20	60	100
$H_2C_2O_4 \cdot 2H_2O$,	g.		8	33	40
Vanadyl sulfate g. (%)		Crude	13 (55)	114.3 (120)	— —
		Purified	4.6 (20)	91 (95.5)	116.8 (98)

The Synthesis of Vanadyl Chloride. — The synthesizing procedure and the reaction process are almost the same as those in the synthesis of vanadyl sulfate, where the sulfuric acid is only replaced by the hydrochloric acid. The reacting solution gradually changes in color from brown to the thick blue characteristic of the vanadyl ion. After the reaction, the solution was filtered and condensed, and the isolation of vanadyl chloride was attempted but in vain. It is, hence, believed that vanadyl chloride itself might be uncrystalline or very easily soluble at an ordinary temperature. Accordingly, the vanadyl ion was determined by the oxidation titration described before and the synthetic yield was calculated from the titration. The results are shown in Table II.

TABLE II. SYNTHETIC CONDITIONS OF VANADYL CHLORIDE

Material		No. 1	No. 2
V_2O_5,	g.	10	50
HCl,	ml.	150 (ca. 5.6 N)	600 (ca. 4.9 N)
$H_2C_2O_4 \cdot 2H_2O$,	g.	8	40
Yield of $VOCl_2$,	%	100	100

The Synthesis of Vanadyl Nitrate.—Vanadyl nitrate seems not to have been isolated; at any rate, its existence has not yet been recognized according to the literature. Although it is impossible to isolate vanadyl nitrate, if the vanadyl ion is synthesized in a solution in which the NO_3^- ion is the sole anion, it can be simply taken as a state in which vanadyl nitrate is dissolved and electrolytically dissociated. This solution can then be used as a starting solution for the electrolysis. By analogy with the syntheses of vanadyl sulfate and vanadyl chloride, the reaction equation is assumed to be:

$$V_2O_5 + H_2C_2O_4 + 4HNO_3 \rightarrow 2VO(NO_3)_2 + 2CO_2 + 3H_2O$$

At 80～90°C, the reaction was carried out in the same way as the synthesis of vanadyl sulfate or vanadyl chloride. During the reaction, the evolution of a red-brown gas was observed and a considerable quantity of unreacted vanadium pentoxide still remained, even when the theoretical weight of oxalic acid was consumed. The reaction was stopped at this point, and the vanadium pentoxide was filtered out. The filtrate showed a thick blue color, indicating the formation of VO^{2+}. The concentration of vanadyl ions was determined by oxidation titrations with potassium permanganate or ceric sulfate, resulting in a good coincidence for the two methods. When vanadium pentoxide (20 g.) in nitric acid (ca. 2.9 N, 300 ml.) was reacted with $C_2H_2O_4\cdot 2H_2O$ (14.3 g.), the yield of vanadyl nitrate calculated from the above results was as follows :

$VO(NO_3)_2$	Found	16 g.
	Calculated	42 g.
	Yield	38%
Unreacted V_2O_5		11 g.

Discussion

Vanadyl Sulfate.—(a) The concentration of sulfuric acid may be diluted down to 20 N as long as the reducing power of oxalic acid is not affected.

(b) It is desirable that the quantity of sulfuric acid be kept at a minimum provided that vanadium pentoxide is kept in the state of suspension.

(c) It is best to add a small excess of oxalic acid (1.2 times of the thoretical weight).

(d) It is desirable that the quantity of water be such that the reaction product is easily crystallized when the solution is condensed and dried (about 95°C) after the reaction.

(e) As for the reaction temperature, it is clear that the threshold temperature for the reduction with oxalic acid is about 70°C. No evolution of carbon dioxide is observed below this temperature, but above 100°C the foaming is very much intensified.

(f) It is naturally desirable to stir the solution as vigorously as possible.

(g) The vanadyl sulfate obtained is stable even at temperatures above 100°C.

Vanadyl Chloride.—(a) The reaction proceeds nearly theoretically.

(b) The reaction does not proceed at temperatures below 60°C. The concentration of hydrochloric acid does not affect the yield if it is in the range of 2 N and above.

(d) As it is difficult to isolate vanadyl chloride, the reaction solution should be directly used for the electrolysis.

Vanadyl Nitrate.—The red-brown gas evolving in the course of the reaction is believed to be nitrogen dioxide or nitrogen sesquioxide resulting from the decomposition of nitric acid. Probably the oxalic acid is partly consumed in decomposing the nitric acid, resulting in the poor yield of vanadyl nitrate.

Electrolytic Reduction Process

As has been described before, in this process the vanadyl salt is cathodically reduced to the V^{2+} state. In this case, VO^{+2} is considered to be reduced first to V^{3+} and then to V^{2+}.

$$VO^{2+}+2H^{+}+e\rightarrow V^{3+}+H_2O\ ;\quad V^{3+}+e\rightarrow V^{2+}$$

The theoretical electric quantity necessary for the above reduction is two faradays. The redox potential of the former system is :

$$E^{\circ}{}_{VO^{2+}/V^{3+}}=+0.337\ \text{V.}^{13)}\quad (25°\text{C})$$

That of the latter has previously been described.

The solution of vanadous salt can also be prepared by chemical reduction using a reducing agent such as zinc amalgam.[14] In the case of photographic use, the electrolytic method is preferable in order to avoid contamination and in order to carry out the continuous regeneration of the developer. It has been reported[4,5] that vanadyl salts, vanadyl sulfate and vanadyl bromide, were electrolyzed with a lead cathode. Schwarzenbach and Sandera[15] also prepared vanadium dichloride using a mercury cathode, and Jones and Colvin[2] obtained vanadium(II) sulfate with a mercury cathode. However, there has been no systematic study of the electrolytic preparation of vanadous salt from the standpoint of electrolytic conditions. Therefore, in the present paper, the influence of various factors, such as (i) the kinds of electrodes, (ii) the kinds of starting compounds and electrolytes, (iii) the current density, and (iv) the acid concentration of catholyte, upon the yield will be described.

Experimental

Materials.—*Vanadyl Sulfate.*—Blue crystals containing 3 molecules of water ($VOSO_4\cdot 3H_2O$) prepared as described above were used. Their purity was determined by cerimetry to be more than 98%.

Vanadyl Chloride.—The compound prepared as described before was used. As it was not crystallized, the solution in hydrochloric acid was directly used for the electrolysis. Its concentration was determined by cerimetry.

Vanadyl Nitrate.—A solution of the compound in nitric acid was used for the electrolysis, and its concentration was determined in the same way as before.

Cathode.—Mercury, lead, copper or stainless steel (hereunder abbreviated as S. S.) was used as a cathode. Except for those of mercury, the electrodes were cylindrical plates provided with a number of

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[13] G. Jones and J. Colvin, *J. Am. Chem. Soc.*, **66**, 1563 (1944).

[14] L. Meites, *J. Chem. Educ.*, **27**, 458 (1950).

[15] G. Schwarzenbach and J. Sandera, *Helv. Chim. Acta*, **36**, 1089 (1953).

small holes (1 cm.ϕ) to help the flow of the electrolyte solution. The circumference, height and area were 21 cm., 6.8 cm. and 121.8 cm^2 respectively. In the case of mercury, the mercury pool at the bottom of the electrolytic cell served as a cathode.

Anode.—As the anode must be acid-proof, lead peroxide and platinum were tested. The surface layer of lead peroxide peeled in the course of a long run, resulting in the contamination of the anolyte, so the platinum anode was finally adopted. The size of the electrode is not directly related to the results of the cathodic reduction, so it is adequate to choose it according to the dimensions of the anode chamber.

Diaphragm.—A cylindrical porous diaphragm was used. In order to avoid the dissolution of the components of the diaphragm, it was first soaked in acid and alkaline solutions and then the weight change of it and its porosity were measured. The diaphragm was treated in the following order: weighing → washing by water → soaking in hydrochloric acid 5% for 24 hr.→washing by water→ soaking in sodium hydroxide 1% for 24 hr.→washing by water→resoaking in hydrochloric acid 5% for 24 hr.→washing by water→drying→weighing. The hydrochloric acid soaking solution was colored somewhat yellow, clearly showing the dissolution of iron. The ratios of the weight change of two tested diaphragms, a and b, before and after the treatment were as follows;

a −0.33%; b −0.35%

The porosity was measured according to the following formula:

$$\text{Porosity} = \frac{\text{Weight(saturated with water)} - \text{Weight(dry)}}{\text{Total volume}}$$

The results obtained from several samples were 25∼35% of porosity.

When these diaphragms were used for electrolysis, the following results were obtained.

(a) There is scarcely any dissolution of diaphragm components.

(b) The separation of the catholyte is perfect, and there is no transference of vanadium ions into the anode chamber.

(c) A part of the anolyte moves into the cathode chamber, and the difference between the levels of the anolyte and of the catholyte becomes 2∼3 cm. However, as the same kind of acid is used for both anolyte and catholyte, no unfavorable effect of this movement is observed except for the change in the concentration of the acid.

Electrolytic Cell.—A 500 cc. beaker was used for the electrolytic cell, as Fig. 1 shows. The diaphragm was placed at the center of the cell for the anode chamber, and the outside part of it constituted a cathode chamber. The cathode chamber was closed with a rubber stopper to protect the V^{2+} ion from air oxidation. The stopper was provided with several small holes for measuring the cathode potential, for a thermometer, for the passage of nitrogen, and for removing the evolved hydrogen.

Electrolytic DC Power Supply.—AC power was selenium-rectified to be used as the DC electrolytic power source. The voltage was adjusted by a slidac on the AC side and by a sliding resistance on the DC side.

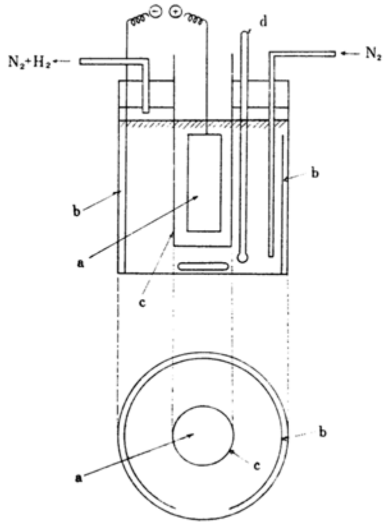

Fig. 1. Electrolytic cell. a, Anode; b, Cathode; c, Diaphragm; d, Thermometer.

Electrolyte.—The three following solutions, (a) a hydrochloric or sulfuric acid solution of vanadyl sulfate, (b) a hydrochloric acid solution of vanadyl chloride, and (c) a nitric acid solution of vanadyl nitrate, served as catholytes, and the same acid was used for the catholyte as for the anolyte.

The acid concentrations of both catholyte and anolyte were kept equal.

When hydrochloric acid or nitric acid was used as an anolyte, stimulative gas evolved; this was removed by an aspirator.

The Possibility of Using V^{3+} Salt as a Starting Material.—If a V^{3+} salt solution exists, there is no need of chemical synthesis and the preparation of developer will be very much simplified. Vanadium trioxide (V_2O_3) is the only V^{3+} compound available on the market. Vanadium trioxide is stable and is almost insoluble in every kind of acid, and the slightly-dissolved components seem to be in a V^{4+} state, judging from the color. On the other hand, V^{3+} precipitates in alkaline solution in the form of vanadium(III) hydroxide. Thus, vanadium trioxide is considered not to be suitable for the starting material in preparing the vanadium developer.

Electrolytic Procedure.—The electrolysis was carried out under strong agitation by a magnetic stirrer. During electrolysis the applied voltage was adjusted so that the current density could be kept constant. The temperature rose with the electrolysis, but it was kept below 30°C by cooling with ice. When vanadyl sulfate or vanadyl chloride was electrolyzed, the catholyte changed its color from blue to green, showing the existence of V^{3+}, and then to the violet of V^{2+}. The hydrogen began to evolve vigorously when the theoretical electric quantity was consumed. When the electric quantity reached twice the theoretical quantity, the electrolysis was stopped and the catholyte was removed into a stoppered flask. The yield was determined by the simultaneous potentiometric titration of V^{2+} and V^{3+}.[16] During electrolysis, the evolved hydrogen protected V^{2+} from air oxidation, so there was no need for nitrogen passage; otherwise, all the procedures should be carried out in a nitrogen atmosphere.

The electrolysis of vanadyl nitrate will be described later.

Results and Discussion

The Influence of the Kind of Electrodes.—The influence of the kind of electrode upon the electrolytic yield was examined in the case of the catholyte of the vanadyl chloride-hydrochloric acid system. The electrolytic conditions were;

$VOCl_2$ 0.2∼0.6 M/l., HCl 1∼3 N, cathode current density, $D_k=1.64$ amp./dm^2. The results are shown in the following table.

Electrode	Yield, %
Pb	82
Cu	62
S. S	25

For the electrolyte of the vanadyl sulfate-sulfuric acid system, the electrolytic conditions were;

$VOSO_4$ 0.1 M/l., H_2SO_4 1 N, and

$D_k=1.6\sim2.0$ amp./dm^2

Those results are as follows:

Electrode	Yield, %
Hg	100
Pb	69

The results show that the mercury cathode gives the highest yield, followed by lead and copper, while the stainless steel gives the lowest. In the latter case, a slight corrosion is observed on the surface of the electrode after the electrolysis; the poor yield may be attributed to the fact that a part of the electrolytic current is consumed for the hydrogen evolution due to the corrosion. Furthermore, taking into account the contamination of the electrolyte, the stainless steel electrode is not preferable in the present electrolysis.

The Influence of the Constitution of the Electrolyte.—From the above results, it was clear that the lead electrode was of practical use, so the influence of the constitution of the electrolyte, namely, the relation between the yield and the kind of acids and electrolyzed materials, was studied in the case of the lead electrode. The results are shown in the following table.

Combination of electrolytes	Yield, %
$VOSO_4$ - H_2SO_4	94
$VOSO_4$ - HCl	72
$VOCl_2$ - HCl	82

The other electrolytic conditions were kept constant as follows:

$D_k=0.82$ amp./dm^2,
acid concentration = 1∼2 N,
concentration of vanadyl salt = 0.1 M/l.

As is clear from the results, the combination of vanadyl sulfate and sulfuric acid gives the highest yield, followed by the combination of vanadyl chloride, hydrochloric acid and vanadyl sulfate - hydrochloric acid. It is concluded that the combination of vanadyl salt and acid gives a higher yield when they possess a common anion.

The Influence of Cathode Current Density (D_k).—The influence of the cathode current density upon the yield, using the lead cathode and the vanadyl sulfate - sulfuric acid electrolyte, the optimum condition so far achieved, was also studied.

The electrolytic conditions were as follows:

Cathode—Pb,		Anode—Pt
Catholyte	$VOSO_4$	0.1 M/l.
	H_2SO_4	1 N
Anolyte	H_2SO_4	1 N

The results are shown in Fig. 2 and in the following table.

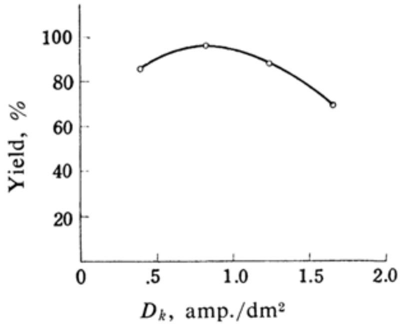

Fig. 2. Relation between the cathode current density (D_k) and the yield.

Current density, amp./dm^2	Yield, %
0.41	85
0.82	94
1.23	87
1.64	69

From the table, it can be seen that the highest yield, 94%, is reached when D_k is about 0.82 amp./dm^2. In general, with the increase of the cathodic current density, the hydrogen over-voltage increases, while the reducing power of the cathode is argumented. However, the results show that, if the current

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[16] Presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

density rises, the yield decreases. This is supposed to be due to the fact that the evolution of the hydrogen in a very acidic solution like the present electrolyte competes with the reduction of vanadium.

The Influence of the Concentration of Sulfuric Acid as Catholyte.—The influence of the concentration of sulfuric acid upon the yield was then studied under the optimum conditions hitherto mentioned, with the lead cathode, the vanadyl sulfate - sulfuric acid electrolyte, and $D_k=0.82$ amp./dm^2.

The electrolytic conditions were as follows:

Cathode—Pb Anode—Pt

$$\text{Catholyte}\begin{cases}\text{VOSO}_4 & 0.1\ \text{M/l.}\\ \text{H}_2\text{SO}_4 & 0.1\sim 8\ \text{N}\end{cases}$$

Anolyte—H_2SO_4, the concentration being the same as that of the catholyte.

The results are shown in Fig. 3 and in the following table.

Concn. of H_2SO_4, N	Yield, %
0.1	89
1.0	94
8.0	87

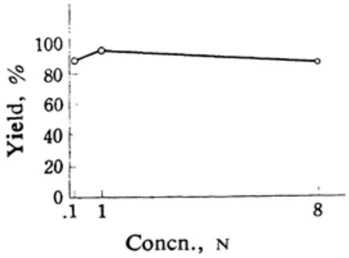

Fig. 3. Relation between the concentration of sulfuric acid as catholyte and the yield.

From the results, it was seen that the concentration of the sulfuric acid in the range of $0.1\sim 8$ N does not exert an important influence upon the yield, the variation of the yield being less than 7%.

Therefore, the influence of the concentration of the sulfuric acid may be taken into account in relation with the stability of the V^{2+} ions dissolved and with their reducing power or developing ability.

According to Charlot,[17] the redox potential of the V^{3+}-V^{2+} system becomes more negative with the increase of pH, so its electrochemical reducing power must argument with the decrease in acidity. Furthermore, according to Jones and Colvin,[2] in a strong acid solution, V^{2+} reduces the hydrogen ion, evolving the hydrogen, and V^{2+} itself is oxidized to V^{3+}.

From the above standpoint, it is best if the acid concentration of the catholyte is low as long as the yield of V^{2+} is not affected.

The Electrolysis of Vanadyl Nitrate.—The electrolysis of the solution of vanadyl nitrate mentioned before was attempted under the same conditions as in the case of electrolysis of vanadyl sulfate or vanadyl chloride.

The electrolytic conditions were as follows:

Cathode—Pb Anode—Pt

$$\text{Catholyte}\begin{cases}\text{VO(NO}_3)_2 & 0.1\ \text{M/l.}\\ \text{HNO}_3 & \text{ca. } 1.3\ \text{N}\end{cases}$$

Anolyte HNO_3 ca. 1.3 N

$D_k=0.82$ amp./dm^2

The consumption of electricity was three times the theoretical value.

In spite of the excessive consumption of electricity, the color of the electrolyte solution remained blue, a color characteristic of VO^{2+} ions, not showing the violet color of V^{2+}. The potentiometric titration of the electrolyzed solution showed a one-step curve corresponding to the redox potential of VO^{2+}/V^{5+}, undoubtedly indicating that there was no formation of V^{2+} or V^{3+}. Accordingly, it seems impossible to prepare V^{2+} electrolytically from vanadyl nitrate.

The reason why the electrolysis of vanadyl nitrate does not proceed is supposed to be due to the fact that cathodically-formed V^{2+} or V^{3+} reacts with the nitric acid, reduces it, and itself returns to the VO^{2+} state.

Conclusion

The Chemical Reduction Process.—(i) The synthesis of vanadyl sulfate by the oxalic acid method proceeds theoretically, obtaining blue crystals containing 3 molecules of the water of crystallization ($VOSO_4\cdot 3H_2O$). The crude yield attains 100%, and the purified one, 98%. (ii) The synthesis of vanadyl chloride also proceeds theoretically, and the yield attains 100%. It is, however, impossible to isolate the vanadyl chloride of the crystalline state. (iii) The synthesis of vanadyl nitrate by the oxalic acid method dose not give satisfactory results, showing a yield as poor as 38%. However, the unreacted V_2O_5 can be recovered up to 90%. (iv) None of the synthesizing reactions mentioned above proceed at all at temperatures below 70°C.

The Electrolytic Reduction Process.—(i) The electrolytic preparation of V^{2+} salt from vanadyl sulfate gives the highest yield, 100%. (ii) When the vanadyl chloride is electrolyzed, the maximum yield obtained is 82%. (iii) In both cases, the conditions required for obtaining the maximum yield are:

Cathode—Lead or mercury

Catholyte—All acids contained the same

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[17] G. Charlot, "L'analyse qualitative et les réactions en solution," Massonet Cie, Paris (1957).

anion as that of vanadyl salt to be electrolyzed.

Concentration of acid—0.1∼8 N
Temperature—Room temperature
Cathodic current density—0.82 amp./dm^2

(iv) Vanadyl nitrate is not reduced electrolytically, and it is impossible to obtain V^{2+} salt from it.

Summary

A systematic study of the preparation of a V^{2+} developer for use in the continuous automatic processing machine has been carried out.

At first the vanadyl salts, such as vanadyl sulfate and vanadyl chloride, were chemically synthesized from vanadium pentoxide with a yield of nearly 100%, while vanadyl nitrate was obtained with a yield of only 38%. The synthesizing method using oxalic acid was considered to be the most advantageous from the standpoint of the succeeding electrolytic process.

Concerning the electrolytic reduction process to obtain V^{2+} salt from vanadyl salt, the influence of the kind of electrodes, the combination and concentration of electrolytes, and the cathodic current density upon the yield has been studied. On the basis of these studies, the optimum conditions for the electrolysis have been established except for vanadyl nitrate.

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