Electrolytic Production of Lead Cyanamide

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Lead cyanamide is an insoluble yellowish colored lead salt of cyanamide, designated as $PbCN_2$ or $Pb(HNCN)_2$ for its molar composition, and has been used fairly widely as anticorrosive pigment and is known to exhibit excellent protective performance, particularly in the field of marine applications.

However, production of the pigment seems to be relatively limited mainly because of its rather high production cost. The lead cyanamide has so far been synthesized through roundabout processing steps *via* intermediate soluble salts of lead such as acetate and nitrate[1] or insoluble lead compounds including litharge, PbO,[2] to provide the source of lead to combine cyanamide radical which usually comes from the leach of nitro-lime. Therefore, the production cost of lead cyanamide becomes substantially higher than those of many other anticorrosive lead pigments such as litharge which can be supplied in most cases *via* much fewer processing steps.

In this work an attempt has been made to establish a straightforward precipitation of lead cyanamide directly starting from metal lead as the source of lead to eliminate the need for the costly intermediate lead compounds, by applying the technique of soluble anode electrolytic process, and some of the important electrolytic variables are investigated to obtain the high grade lead cyanamide product.

Experimental

Materials. A commercial fertilizer grade nitrolime whose cyanamide content as $CaCN_2$ was about 60% was leached with water and the leached solution was desulfurized by adding ferrous sulfate according to the conventional method. The concentration of $CaCN_2$ was controlled to from several to 10 g per liter of the purified leach. Sodium chlorate was then added as solubilyzer of lead anode in an amount of 10—80 g per liter and the final solution was provided as the electrolyte.

High purity lead of more than 99.9% Pb was cast into the form of electrodes with dimensions of 4 cm × 7 cm × 1 cm. The plate of anode was placed in between two plates of cathodes with anode-cathode distance of 5 cm.

Procedures. Electrolysis was carried out with a 2-liter experimental electrolytic cell with continuous circulation of electrolyte with fresh supply of cyanamide to maintain as homogeneous concentration as possible throughout the electrolytic run. The amperage was adjusted in the range of 1 to 3.5 A/dm^2, and the duration of electrolysis per each run was 8 hr.

Content of nitrogen as cyanamide form in the lead cyanamide precipitate was analyzed by the use of silver

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[1] *E.g.*, E. Blasiak and Z. S. Matsuszewski, Pol. Pat. 42862 (1960).

[2] V. Koutnik and V. Novak, *Chem. Prumsi*, **9**, 18 (1959), *Chem. Abstr.*, **58**, 17445 (1959).

cyanamide precipitation method.[3-6] A quantity of 0.5 g of the lead cyanamide sample was dissolved with dilute nitric acid and the solution was passed through an ion exchange column which contained H^+-form Amberlite IR-120 resin to replace lead ion of the solution with hydrogen ion. Ammoniacal solution of silver nitrate was then added to the effluent to secure the cyanamide into the form of silver cyanamide, which was then dissolved with dilute nitric acid and the content of the cyanamide was determined by titrating the combined silver according to the Volhard method with a potassium thiocyanate solution using ferro-ammonium alum as indicator.

As for the alternative in expressing the composition of lead cyanamide, Costa and Bolis-Cannella[7] demonstrated that the analytical composition of their laboratoy-produced pigment was Pb 81.760, N 9.830, C 4.282, H 0.144, O and undetermined impurities of inorganic nature 3.984%, which was very near to $PbCN_2$ rather than $Pb(HNCN)_2$. The thermal work[8] on silver, copper, lead, and cadmium cyanamides exhibited that these compounds developed N, $(CN)_2$, CO_2 or CO when heated in air, and partially polymerized $(CN)_x$ when heated *in vacuo*,, respectively, with no decomposition product containing H. A recent work of Sole and Yoffe[9] to determine the nature of the bonds in the sodium, thallium, mercury, and lead cyanamides also showed that while sodium cyanamide was an ionic solid, silver and lead cyanamide salts were covalent ones. Accordingly, the composition of the product obtained in the present work was also expressed in terms of $PbCN_2$ basis instead of $Pb(HNCN)_2$.

Results and discussion

A series of experimentations have been carried out varying the composition of electrolyte and the current density, and the $PbCN_2$ content of the electrolytically obtained product is enlisted in Table 1. It is observed that the high grade lead cyanamide, the $PbCN_2$ content of which is more than 90%, has been obtained through one-step electrolytic process directly starting from the metal lead being attacked by the electrolyte composed of calcium cyanamide, supplier of CN_2^{-2} ion, and sodium chlorate, solubilyzer of the lead, with cell voltage of about 2—3 V.

It is seen that the increase in sodium chlorate concentration of the electrolyte increases the $PbCN_2$ content of the electrolytically precipitated product as illustrated in Fig. 1. The higher anodic current

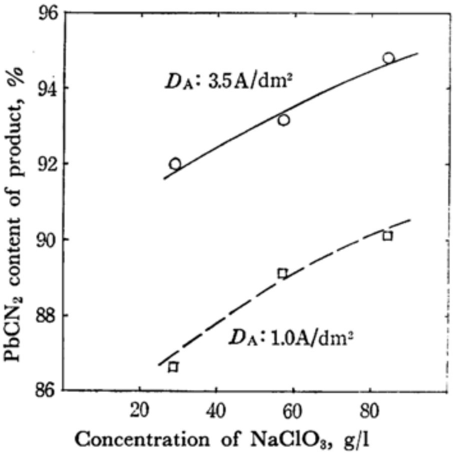

Fig. 1 Amount of $NaClO_3$ added to the electrolyte of 8 g $CaCN_2$/l *versus* grade of lead cyanamide obtained, in terms of applied current density.

TABLE 1. ELECTROLYTIC PRECIPITATION OF LEAD CYANAMIDE

Run No.	Composition of Electrolyte, g/*l*		Current Density D_A, A/dm²	Cell Voltage, *v*			$PbCN_2$ Content of Product, %
	$CaCN_2$	$NaClO_3$		Initial	Final	Average	
1	8.0	28.0	1.0	1.7	1.8	1.8	86.6
2	8.0	28.0	3.5	2.3	3.0	2.2	92.0
3	8.0	56.0	1.0	1.5	2.1	1.8	89.5
4	8.0	56.0	3.5	2.2	3.2	2.7	93.2
5	8.0	84.0	1.0	1.6	1.9	1.8	90.7
6	8.0	84.0	3.5	2.3	3.1	2.7	94.8
7	4.0	14.0	1.0	2.4	2.8	2.6	86.7
8	4.0	14.0	3.5	5.2	5.4	5.3	92.9
9	4.0	28.0	1.0	2.0	2.3	2.2	87.4
10	4.0	28.0	3.5	3.8	3.8	3.8	92.3
11	4.0	42.0	1.0	2.0	2.2	2.2	87.9
12	4.0	42.0	3.5	2.9	3.3	3.1	92.0

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[3] C. Brioux, *Ann. Chim. Anal.*, **15**, 341 (1911).

[4] G. Grube and J. Krüger, *Z. Angew. Chem.*, **27**, 326 (1914).

[5] L. A. Pinck, *Ind. Eng. Chem.*, **17**, 459 (1925).

[6] H. Kittel, "Pigmente," Wiss. Verlagsg. m. b. H., Stuttgart (1960), p. 722.

[7] D. Costa and C. Bolis-Cannella, *Ann. chim.*, **43**, 769 (1953).

[8] C. Bolis-Cannella, *Ann. chim.*, **44**, 1064 (1954).

[9] M. J. Sole and A. D. Yoffe, *Proc. Roy. Soc.*, *Ser. A*, **277** (1371), 498 (1964).

density produces, the higher grade of lead cyanamide, *i. e.,* 92—95% of $PbCN_2$. The balance of the constituent is not yet definitely identified, however it may probably exist in the form of a basic oxide of lead. The values of $PbCN_2$ content in Table 1 is remarkably higher in comparison with those of the commercially available products marketed elsewhere including a sample from overseas which were found to be in the range of 82—84% $PbCN_2$ by the same analytical method.

It is to be noted, however, as is seen from Fig. 2, that when the original concentration of calcium cyanamide in the electrolyte is low, the increase of sodium chlorate will rather lower the grade of the pigment especially under higher current density. This is understood in such a way that the lead ion which is supplied from the anode in relatively excess amount over the cyanamide ion present in the electrolyte forms basic salts of lead to coprecipitate and dilute lead cyanamide content for the run.

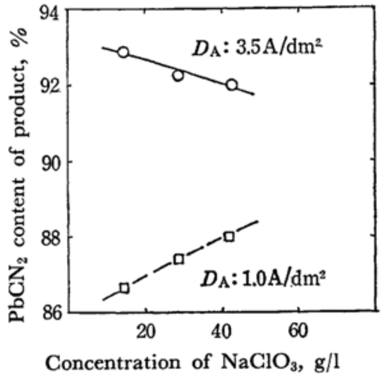

Fig. 2. Amount of $NaClO_3$ added to the electrolyte of 4 g $CaCN_2$/l versus grade of lead cyanamide obtained, in terms of applied current density.

The runs No. 1 through No. 6 and No. 7 through No. 12 in Table 1 divide total runs of experiment into two groups of $CaCN_2$ concentrations, *i. e.,* 8 and 4 g/*l*, while having same mixing ratios of $CaCN_2$ and $NaClO_3$ for the each adjacent runs respectively. It is interesting to note that the $PbCN_2$ content of a product obtained with a given $CaCN_2$-$NaClO_3$ combination will not depend solely on the mixing ratio of $CaCN_2$ and $NaClO_3$ even under a same anodic current density, but is largely determined by the concentration of the existing $CaCN_2$. It is seen that the higher concentration of $CaCN_2$ in the electrolyte gives rise to the higher grade of lead cyanamide.

It should be pointed out, therefore, that the proper choice of conditions is necessary to run favorable electrolysis of high quality lead cyanamide pigment. Continuation of electrolysis down to a too low concentration of $CaCN_2$ with high current density should cautiously be avoided.

Summary

Electrolytically precipitating process has been examined to obtain anti-corrosive lead cyanamide pigment, eliminating the need for the conventional intermediate lead compounds such as litharge. A soluble electrolysis of metallic lead anode has been carried out with calcium cyanamide electrolyte which contains a proper amount of sodium chlorate as a solubilyzer of anode. The electrolytically operated product was of a higher grade of lead cyanamide of 92—95% $PbCN_2$, in comparison with the conventionally available pigment of 82—84% $PbCN_2$. The $CaCN_2$-$NaClO_3$ ratio, $CaCN_2$ concentration and anodic current density have been found to be of major importance which primarily govern the quality of product.