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Improved Manufacturing Synthesis of Phosphorus Sulphochloride

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A practical, improved manufacturing synthesis of phosphorus sulphochloride has been developed. The one-step process with continuous 67 times repeatable batches achieved 95 % overall isolated yield using *n*-tributylamine as catalyst.

Key Words: Phosphorus trichloride, *n*-Tributylamine, Phosphorus sulphochloride, Process.

INTRODUCTION

As the important pharmaceutical starting material, phosphorus sulphochloride has been widely used in production of many pesticides, such as organophosphorus pesticides. Literatures and patents have reported its manufacturing synthesis since a century before[1]. The classical approaches for the preparation use sulfur reacting with phosphorus trichloride under refluxing to produce phosphorus sulphochloride. German Bayer[2] reported in 1960 that the reaction was catalyzed by presence of carbon preferably activated under reducing conditions with potassium sulphide, and also accelerated by addition of phosphorus sulphochloride at the beginning of reaction. However, the yield was not very good and also the solid carbon could cause problem in workup procedure while in production. Frehden *et al.*[3] used new catalyst to take place of activated carbon. The metallic aluminum or aluminum alloy were employed to this process also with phosphorus sulphochloride as medium and moderator at the commencement of reaction. From industrial point of view, the disadvantage of the use of metallic aluminum or aluminum alloy lies in disposal of large tons of wastes, especially the solid wastes, such as Al_2S_3, FeS, $Al_2(SO_4)_3$, which cause serious pollution on environment. To remove this problem, in 1995, Bayer corporation firstly reported[4] that liquid tertiary amine, typically, methylpyridine could be used to promote the reaction between phosphorus trichloride and sulfur to give phosphorus sulphochloride with cumulative yield of 79-96.2 % after recycling 10 batches. In this preparation, 0.16 eq of amine was used and the heel formation needs 9 h. After 6 years, based on previous process, Bayer corporation discovered[5] an improved methodology in which nitroxide radical, typically, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was employed as catalyst along with 0.16 eq of tertiary amine to promote the formation of phosphorus sulphochloride, therefore, the time for heel formation was reduced to 3 h. After recycling 3 batches, the cumulative yield was achieved to 91.6 %.

Considering industrial applicability, we intended to elaborate an efficient and robust process for phosphorus sulphochloride. In this article, we like to present an improved manufacturing synthesis of phosphorus sulphochloride.

EXPERIMENTAL

General procedure for preparing phosphorus sulphochloride: The mixture of phosphorus sulphochloride (84.75 g, 500 mmol), sulfur (22.4 g, 700 mmol) and *n*-tributylamine (7.4 g, 40 mmol) was heated to 120 ºC with effective stirring. To this mixture was added dropwise the phosphorus trichloride (70 g, 509.72 mmol) during 1.5 h. After addition, the reaction was refluxing for 1.5 h and then phosphorus sulphochloride was collected between 126 to 130 ºC by distillation (the yield of phosphorus sulphochloride was calculated here). After distillation was almostly completed, the first recycle started by addition the mixture of sulfur (16.0 g, 500 mmol) and phosphorus sulphochloride (84.75 g, 500 mmol). Then phosphorus trichloride (70 g, 509.72 mmol) was added dropwise during 1.5 h, and meanwhile, the trichloride phosphoride was distilled. In later continuous recycles, above procedure starting from adding mixture of sulfur (16 g, 500 mmol) and trichloride phosphoride (70 g, 509.72 mmol) was repeated to give 67 continuous batches. The purity of trichloride phosphoride was 98-98.5 % by GC. The single and cumulative yields were summarized in Table-1.

TABLE-1
FORMATION OF PHOSPHORUS SULPHOCHLORIDE CATALYZED BY *n*-TRIBUTYLAMINE

Batch number	*n*-Tributyl amine (mol)	PCl_3 (mol)	Sulfur (mol)	Single yield (%)	Cumulative yield (%)
Heel formation	0.04	0.50972	0.70	85.95	85.95
Recycle #1	0.00	0.50000	0.50	87.37	86.67
Recycle #2	0.00	0.50000	0.50	88.64	87.33
Recycle #3	0.00	0.50000	0.50	90.35	88.08
Recycle #4	0.00	0.50000	0.50	90.56	88.58
Recycle #5	0.00	0.50000	0.50	91.66	89.09
Recycle #6	0.00	0.50000	0.50	89.91	89.21
Recycle #7	0.00	0.50000	0.50	90.56	89.38
Recycle #8	0.00	0.50000	0.50	91.41	89.60
Recycle #9	0.00	0.50000	0.50	89.69	89.61
Recycle #10	0.00	0.50000	0.50	90.44	89.69
Recycle #11	0.00	0.50000	0.50	90.70	89.77
Recycle #12	0.00	0.50000	0.50	92.37	89.97
Recycle #13	0.00	0.50000	0.50	94.53	90.30
Recycle #14	0.00	0.50000	0.50	89.43	90.24
Recycle #15	0.00	0.50000	0.50	94.24	90.49
Recycle #16	0.00	0.50000	0.50	93.22	90.65
Recycle #17	0.00	0.50000	0.50	95.12	90.90
Recycle #18	0.00	0.50000	0.50	92.58	90.99
Recycle #19	0.00	0.50000	0.50	91.96	91.04
Recycle #20	0.00	0.50000	0.50	91.58	91.06
Recycle #21	0.00	0.50000	0.50	91.36	91.08
Recycle #22	0.00	0.50000	0.50	96.76	91.32
Recycle #23	0.00	0.50000	0.50	92.28	91.36
Recycle #24	0.00	0.50000	0.50	95.72	91.54
Recycle #25	0.00	0.50000	0.50	95.67	91.70
Recycle #26	0.00	0.50000	0.50	94.24	91.79
Recycle #27	0.00	0.50000	0.50	96.61	91.96
Recycle #28	0.00	0.50000	0.50	94.28	92.04
Recycle #29	0.00	0.50000	0.50	97.91	92.24
Recycle #30	0.00	0.50000	0.50	93.54	92.28
Recycle #31	0.00	0.50000	0.50	98.15	92.46
Recycle #32	0.00	0.50000	0.50	97.13	92.60
Recycle #33	0.00	0.50000	0.50	96.17	92.71
Recycle #34	0.00	0.50000	0.50	96.87	92.83
Recycle #35	0.00	0.50000	0.50	95.68	92.91
Recycle #36	0.00	0.50000	0.50	97.39	93.03
Recycle #37	0.00	0.50000	0.50	96.61	93.12
Recycle #38	0.00	0.50000	0.50	97.96	93.25
Recycle #39	0.00	0.50000	0.50	101.09	93.44
Recycle #40	0.00	0.50000	0.50	98.72	93.57
Recycle #41	0.00	0.50000	0.50	97.83	93.67
Recycle #42	0.00	0.50000	0.50	98.79	93.79
Recycle #43	0.00	0.50000	0.50	98.35	93.89
Recycle #44	0.00	0.50000	0.50	100.76	94.05
Recycle #45	0.00	0.50000	0.50	101.13	94.20
Recycle #46	0.00	0.50000	0.50	97.47	94.27
Recycle #47	0.00	0.50000	0.50	101.39	94.42
Recycle #48	0.00	0.50000	0.50	100.97	94.55
Recycle #49	0.00	0.50000	0.50	98.00	94.62
Recycle #50	0.00	0.50000	0.50	100.77	94.74
Recycle #51	0.00	0.50000	0.50	99.06	94.83
Recycle #52	0.00	0.50000	0.50	98.53	94.90
Recycle #53	0.00	0.50000	0.50	98.78	94.97
Recycle #54	0.00	0.50000	0.50	101.22	95.08
Recycle #55	0.00	0.50000	0.50	98.92	95.15
Recycle #56	0.00	0.50000	0.50	101.35	95.26
Recycle #57	0.00	0.50000	0.50	98.42	95.31
Recycle #58	0.00	0.50000	0.50	98.38	95.36
Recycle #59	0.00	0.50000	0.50	100.71	95.45
Recycle #60	0.00	0.50000	0.50	101.29	95.55
Recycle #61	0.00	0.50000	0.50	99.68	95.62
Recycle #62	0.00	0.50000	0.50	100.84	95.70
Recycle #63	0.00	0.50000	0.50	99.33	95.76
Recycle #64	0.00	0.50000	0.50	99.18	95.81
Recycle #65	0.00	0.50000	0.50	100.64	95.88
Recycle #66	0.00	0.50000	0.50	99.75	95.94

RESULTS AND DISCUSSION

In the first two patents[2,3], around 40 % of phosphorus sulphochloride was used as medium and moderator at the beginning of reaction. In the later reports[4,5], when using new catalysts, without addition of phosphorus sulphochloride at the commencement of reaction, then long hours for heel formation is needed and recycling number of times are limited. Especially, after almost all phosphorus sulphochloride is collected every times, the "naked" amine left in vessel risks being oxidation, this condition could cause catalyst inactivation, thus, result in very limited continuous bathes. We suppose that phosphorus sulphochloride in reaction probably could protect amine and could not only prolong the life of catalyst, but could also benefit the conversion of sulfur, so could accelerate the reaction. Therefore, in our process, around 1 eq of phosphorus sulphochloride was added into initial reaction. Meanwhile different amount of *n*-tributyl amine was investigated and found that 0.078 eq of amine was actually enough to catalyze reaction in continuous 67 batches (Table-1), because both single yield of each batch and cumulative yield of 67 batches did not change much. Furthermore, the GC purity of phosphorus sulphochloride has been maintained over 98 % during 67 batches.

On the basis of the analysis of all data in Table-1, two figures (Figs. 1 and 2) were given to explain the relationship between two kinds of yield and reaction number of times. The result showed that the two kinds of yield in later batches tended to more and more higher than that of former batch. The single yield for some batches was almost reached to theoretical yield (Fig. 1), which indicated high efficiency of the catalyst. The cumulative yield of later batch always higher than previous one and was reached over 95 % after recycling 54 batches, which also indicated activity of the catalyst in reaction mixture has been maintained very good even after recycling 54 batches (Fig. 2). The single yield difference between two near batches also tended to more and more minor (Fig. 3), this could prove stability of the process, which is very important for manufacturing production.

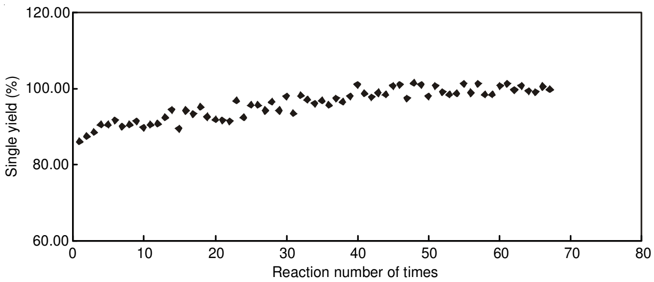

Fig. 1. Relationship between single yield and reaction number of times

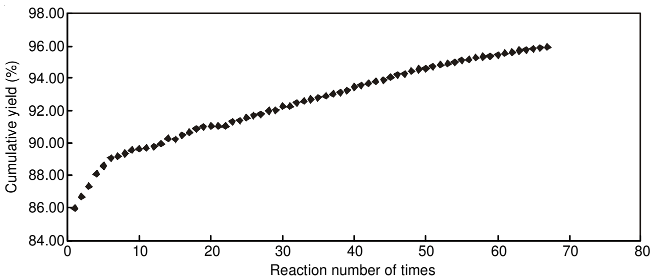

Fig. 2. Relationship between cumulative yield and reaction number of times

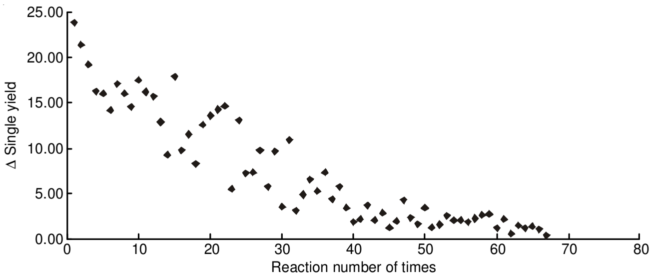

Fig. 3. Relationship between single yield difference of two near batches and reaction number of times

Conclusion

This research presented one practical and efficient process for manufacturing synthesis of phosphorus sulphochloride, in which much less amount of catalyst was used and this is cost-effective for production. Furthermore, the materials inside the reaction vessel has been kept good fluidity during continuous process even after recycling 67 batches, therefore, it could be easy to clean the reaction apparatus after the preparation is finished and this is actually valuable for production in factory.

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