UNCLASSIFIED

"NITRATION REACTIONS OF SHELL SPRAY BASE UNDER
PUREX WASTE RECOVERY PROCESS CONDITIONS"

HW-26517

by

R. M. Wagner
Chemical Research
Separations Technology Unit
TECHNICAL SECTION

CLASSIFICATION CANCELLED
DATE MAR 4 1957 <i>ml</i>
For The Atomic Energy Commission
<i>H. F. Canale</i>
Chief, Declassification Branch

December 5, 1952

Photostat Price \$	<u>3.30</u>
Microfilm Price \$	<u>2.40</u>
Available from the Office of Technical Services Department of Commerce Washington 25, D. C.	

HANFORD WORKS
RICHLAND, WASHINGTON

OPERATED FOR THE ATOMIC ENERGY COMMISSION BY THE GENERAL ELECTRIC COMPANY
UNDER CONTRACT NUMBER W-31-109-ENG-52.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

UNCLASSIFIED

CLASSIFIED

-3-

HW-26517

INTRODUCTION

In the Purex Process the various aqueous process waste streams are combined, concentrated, and 60% nitric acid is recovered from the vapor. It has been assumed that the hydrocarbon diluent, i.e., Shell Spray Base, will be readily steam distillable from these aqueous waste streams in accord with its known steam distillation properties. On the other hand, should nitration reactions occur in the vapor phase at sufficiently rapid rates, and should the resulting nitration products not readily steam distill, two matters might then assume importance: (1) possible explosion during operation and (2) possible deposit of potentially explosive nitro compounds in the underground storage tanks.

Experiments have been performed to characterize the types of nitro compounds which might be formed by reaction of Shell Spray Base with nitric acid, their process path, and to determine the extent of their formation, if any, under process conditions.

SUMMARY

The instability of Shell Spray Base to nitration, under conditions to prevail in the plant, presents neither a disposal nor a safety problem. The entrained Spray Base in the aqueous wastes will be flashed to the fractionator overhead to the extent of greater than 99.5% and will hence go to crib. The amount of nitration during continuous operation of a simulated plant in the laboratory is estimated to vary from 0.01% to 0.001%. In the plant, which is expected to operate with a much lower entrainment factor than was assumed in these experiments, the decomposition products should be negligible in effect as well as in amount. These decomposition products will not remain in the concentrators or fractionator, as they appear to be flashed to the overhead in the same manner as is the Spray Base. The storage of waste, containing small amounts of nitro compounds as their sodium salts, presents no hazard inasmuch as such sodium salts are known to be stable.

REACTIONS UNDER TOTAL REFLUX

To simulate definitely off-standard conditions, e.g., those wherein the continuous distillation of vapor does not prevail, two experiments were performed in which either 50 ml of 30% TBP-Spray Base(IAX) or 50 ml of Spray Base were refluxed with 650 ml of 8 M HNO_3 for a period of four hours. Under these severe conditions heavy nitration was observed with orange coloration of the organic layer and evolution of oxides of nitrogen. On the other hand, a flash distillation of 50 ml of Spray Base from 650 ml of 8 M HNO_3 was performed in a control experiment in which the Spray Base steam distilled completely during a period of three hours, with an aqueous/organic volume ratio of 10:1, and the steam distilled Spray Base remained clear in color.

The two phase systems were extracted in each instance with 100 ml of carbon tetrachloride and the carbon tetrachloride phase extracted with 180 ml of 2 M NaOH. The caustic extracts were then made up to volume in 500 ml dilution flasks using 2 M NaOH. After suitable dilution (1:100) the final dilutions were scanned in the ultra-violet from 230-400 millimicrons using 2 M NaOH as a blank.

DECLASSIFIED

DECLASSIFIED 8-23-2

As the nitro compounds were originally contained in 50 ml of Shell Spray Base, the dilutions described above gave an over-all dilution factor of 1:1000 for the solutions studied. See Figure 3 for these absorption data.

SIMULATION OF PLANT DISTILLATION

To simulate the continuous nitric acid recovery in the plant, shown on Figure 1, a laboratory set-up, as shown in Figure 2, was operated for a period of twenty hours. Inasmuch as the interest was in the stability of the Spray Base, and not in decontamination factors, only one acid concentrator unit was used in the laboratory. To simulate severe entrainment conditions, the flow of Spray Base was set at 1% of the "IWD" rate. Plant entrainment is expected to be approximately 0.1% under proper operating conditions.

The operational data were as follows:

<u>Type Solution</u>		<u>Volume (ml.)</u>
2.0 M HNO_3	feed added	5500
.01 M HNO_3	overhead	4700
13.2 M HNO_3	produced	800
	Spray Base added	55
	Spray Base overhead	54.8

Previous to start-up the boiler pot was charged with 1600 ml of 8 M HNO_3 and the fractionator pot was charged with 500 ml of 14 M HNO_3 . The flow rate of 2 M HNO_3 feed was maintained at 270-280 ml/hr and the Spray Base flow was set at 2.5-3.0 ml/hr. The Spray Base was observed to distill with the overhead 0.01 M HNO_3 as a clear supernate. Essentially complete recovery of the Spray Base was thus obtained and the volume discrepancy is easily accounted for by small experimental error and/or solubility of Spray Base in the 0.01 M HNO_3 .

After the twenty hour operational period was concluded, the items listed below were extracted with 100 ml of carbon tetrachloride and the carbon tetrachloride phases treated as before with 2 M NaOH and made up in 200 ml dilution flasks with 2 M NaOH. The ultra-violet absorption data for these solutions are shown on Figure 4.

<u>Type Solution</u>	<u>Volume (ml.)</u>
0.01 M HNO_3 taken overhead.....	4700
13.2 M HNO_3 taken off during run.....	800
9.0 M HNO_3 in concentrator pot at shut-down	1650
14.6 M HNO_3 in fractionator pot at shut-down	510
16.0 M HNO_3 commercial grade.....	800

DISCUSSION OF EXPERIMENTAL DATA

Reflux Experiments and Flash Distillation Control

The caustic extract of the two reflux experiments was dark red in color which indicated complex mixtures of nitro compounds. The nitro compounds, which were originally contained in 50 ml of Spray Base, were diluted by an over-all factor of 1:1000 in order to obtain relevant ultra-violet absorption data.

823-3

The spectra of these two solutions exhibited high absorption at 330-333 millimicrons which is indicative of salts of alkanenitrolic acids. High absorption shown in the range 290-310 millimicrons is attributable to mononitroalkanes and/or the nitrate ion present. No evidence of dinitroalkane salts, which exhibit an absorption maximum at 382-385 millimicrons, was found in the two reflux samples. The spectrum of the flash distillation control sample showed a faint absorption maximum at 380-383 millimicrons. If this were assumed to be produced by the sodium salt of a dinitroalkane species, the intensity of this peak would indicate less than .09% decomposition of the original Spray Base.

It is not possible to state with certainty, in the case of the two reflux experiments, how much of the Spray Base decomposed to either mononitroalkanes and alkanenitrolic acids. The high absorption of nitrate ion, which was present because of entrainment during the carbon tetrachloride extraction, in the same absorption range precludes this possibility. (See Figure 6). No further effort was made to isolate or identify species produced in the reflux experiments.

Laboratory Simulated Plant Samples and Commercial Nitric Acid Control

The caustic dilutions of the continuous run samples were amenable to examination in the ultra-violet without further dilution, hence the dilution factor in these samples was only 4 compared to 1000 with the reflux samples. The spectrum of the extract of the 0.01 M HNO_3 , which contained greater than 99.5% of the Spray Base introduced into the system, is distinctly different from the spectra of the other samples obtained in the run. This overhead extract is similar to the flash distillation control sample discussed above, except for the fact that the maximum intensity at 380-384 millimicrons represents not more than 0.001% decomposition. The three highly acidic solutions yielded caustic extracts which show spectra in the ultra-violet distinctly similar to the commercial nitric acid extract used as a control. The difference in intensities, quite small indeed, of the four similar spectra, is attributed to the varying amounts of nitric acid entrained in the carbon tetrachloride during the isolation procedure. This is illustrated by the sodium nitrate absorption curves shown in Figure 5.

It is not possible to draw any conclusions concerning the presence of mononitroalkanes in the Spray Base overhead extract or in the other three extracts studied. This is because mononitroalkane salts absorb in the ultra-violet (see Figure 6) at 233 and 300 millimicrons respectively. The sodium nitrate present blocks off all absorption below 245 millimicrons and absorbs strongly at 303 millimicrons.

823-4

FIGURE NO. 1
Purex Nitric Acid Recovery Process

FIGURE NO. 2
SCHEMATIC OF LABORATORY APPARATUS.

DECLASSIFIED

FIGURE NO. 4

"Ultra-violet Spectra of Continuous Run Samples in 2M NaOH."

- Commercial 70% Nitric Acid.
- △ 13.2M HNO_3 produced by fractionator.
- 00.01M HNO_3 overhead from fractionator.
- 9.00M HNO_3 in concentrator pot at shut-down.
- 14.60M HNO_3 in fractionator pot at shut-down.

2.5

Figure No. 6

Absorption in the Ultra-violet
of Mononitroisobutane in 2M NaOH

- A 0.0002M
- B 0.0001M
- C 0.00002M
- D 0.0033M

Above solutions follow
BEER'S LAW

CONFIDENTIAL
-12-

HW-26517

REFERENCES

1. HW-24763 Figure 5 dated 6-16-52; R. Tomlinson & F. W. Woodfield.
2. HW-5201-4 R. M. Wagner, SECRET Notebook.

R. M. Wagner

R. M. Wagner

DECLASSIFIED

ABSTRACT

Experiments were performed to characterize the types of nitro compounds that might be formed by reaction of Shell Spray Base with nitric acid, to determine the extent of their formation, if any, and their path under conditions of nitric acid recovery in the Purex Process.

It is concluded that the instability of Shell Spray Base to nitration, under conditions to prevail in the plant, presents neither a disposal problem nor a safety problem.

RECEIVED
DEC 22 1961
300 AREA
CLASSIFIED FILE

DECLASSIFIED

823-12