This invention relates to a method and composition for dissolving electroplated metals by chemical action and, in particular, it is concerned with the selective solution of nickel which has been electro-deposited on a basis metal.

In any electroplating plant a serious economic problem is centered around the recovery of those plated articles which have imperfections, discolorations, poor adhesion or other non optimum characteristics of the plated film which make them unmarketable. The recovery of the basis article by separating the plated metal from it is of prime importance in the electroplating field because of the value of the article being plated. Conventional methods of removing such faulty plates have included a variety of techniques. In application filed July 1, 1957, Serial No. 668,858, issued May 24, 1960, as United States Patent No. 2,937,940, we have described an improved method of effecting recovery of plated articles.

The variety of prior art methods being practiced emphasizes the importance of the problem and, to some extent, the deficiencies of specific methods proposed. That is, none of the compositions in use in the art is sufficiently selective and safe for use in the removal of plated films from commonly used base metals. The strong acids are corrosive to practically every metal and the etched surface must be refinished after removal of the electro deposited plate. Electrolytic oxidation of the plated metal is also quite non-selective, because the voltages used cannot be made completely selective and because the electrolyte is inherently corrosive. The prime function of the current is to speed the reaction and the metal involved almost invariably forms a soluble salt which is dissolved in the electrolyte or which later precipitates as a sludge.

Chemical oxidation by strong oxidizing agents in the presence of caustic, cyanide or acid has serious drawbacks because of the alkalinity, acidity and instability of the solutions. The base metals such as aluminum, zinc, lead, or commonly used alloys are badly corroded by acid, caustic or cyanide. Fundamental in any of the existing operations also is the risk involved in using the very highly toxic cyanide in the nickel and copper plating shop, where most plating is done from acid solutions.

It is, therefore, a basic object of this invention to provide a nickel stripping solution for use in the reclaimation of nickel plated objects, the solution being characterized by its high degree of selectivity for the removal of nickel deposits from basis metal surfaces, by its capacity for the avoidance of poisoning of the nickel bath, and by the minimization of corrosion and damage to the basis metal.

Other objects and advantages of the invention will in part be obvious and in part appear hereinafter.

In accordance with this invention, the improved selective stripping system is characterized by its combination of nitro organic compounds and ammonium salts in water or water miscible solvents in combination such that ammonia is released in solution in the stripping operation. More specifically the stripping medium is composed of a combination of active components, used in water solution, the first component being an aromatic nitro organic compound containing one or more nitro groups, or mixture of nitro compounds, or a nitroaliphatic compound, or mixture of nitrohalogenics, wherein the aliphatic radical contains from one to about six carbon atoms; the second component being an ammonia salt of an acid such that the ammonia can be released by alkali; the third component of the system being a source of sulfur ion of valence —2. To increase the water solubility of the nitro organic component in water it may carry other substituents such as hydroxyl groups, carboxylic groups, phosphonic acid groups, or sulfonic acid groups or an organic solvent-water system may be used.

Commonly nickel plates are put on copper bases and in such situations it is almost inevitable that the conventional stripping bath becomes contaminated with copper ions. Copper ions have an extraordinary catalytic effect in poisoning the stripping bath.

The stripping reaction is a direct stoichiometric one between the nickel of the plate and the nitro-organic compound in the bath. Economical efficient stripping therefore demands that this reaction be controlled to make it relatively fast and uniform in its speed so that substantially spent solutions will have a useful residual life. As an accelerator of the reaction of the nickel on the nickel plate and also as an ingredient to prevent the poisoning of the solution by copper, we include in the solution a compound capable of providing sulphur ions in a valence of —2. By incorporating such amounts, as much as 1 percent by weight, of the sulphide ion producing compound in the mixture, the medium is modified sufficiently to prevent its being poisoned by traces of copper and to accelerate its rate of nickel stripping. Sodium sulfide is, of course, the preferred source of the ion; other sulfides such as potassium will do; organic sulfur compounds which yield the ion are also useful, typical ones being diethyl thiamium disulfide and trihio-carbonates.

Suitable nitro compounds are: o-, m-, p-nitrochlorobenzenes and mixtures thereof; o-, m-, p-nitrobenzoic acids and mixtures thereof and nitrobenzene sulfofonic acids and mixtures thereof; o-, m-, p-nitroanilines and mixtures thereof; o-, m-, p-nitrophenols and mixtures thereof. Other aromatic nitro compounds suitable for use in accordance with this invention may be found listed in United States Patent 2,698,781 and United States Patent 2,649,361.

The nitroparaffins, relatively ineffective as a group, are preferably those of low molecular weight, which have some solubility in water and which are essentially non-volatile. Thus, the nitropropanes, nitrobutanes, nitropentanes, mono, di and tri substituted, are useful.

Ammonium compounds of either organic or inorganic acids may be used, such as ammonium carbonate and ammonium bicarbonate; ammonium sulfate and ammonium bisulfate; ammonium phosphate, ammonium bi-phosphate, ammonium di-acid phosphate; ammonium nitrate; ammoniumchloride. Ammonium salts of organic acids are also useful; for example, ammonium citrate, tartrate, oxalate, lactate, acetate, propionate, benzoate, phthalate, maleate, etc., may be used; and also ammonium salts, of such amino acids as nitrolactic acid, ethylenediaminetetraacetic acid, diethylenetriaminopteracetic acid salts. In certain situations where the handling of ammonia as such can be tolerated, some of the ammonium salt can be replaced by ammonia solution. It should be understood that the purpose of the ammonia is to complex the Ni ion as rapidly as it is brought into solution. Urea is useful in the bath as a basic compound of ammoniacal nature.

Thus, the bath consists essentially of a solution containing an aromatic or aliphatic nitro compound, together with a caustic alkali which raises the pH into the range.
3,245,780

from about 6 to about 11, so that ammonia is released from the salt to give a high concentration of ammonia ions in solution for efficient operation.

It is fundamental to the process to maintain the solution basic and also to regulate its composition to permit operation at relatively high temperatures. The high temperatures accelerate the stripping action. Where operation at a temperature materially above room temperature is contemplated, i.e., above about 35°C, the ammonia present is released and consumed in complexing nickel as the nickel passes into solution.

The stripping system may have a pH ranging from about 7.5 to a pH of about 11, and the amount of caustic used is related to ammonia need. In utilizing the material in accordance with the invention, the article may be dipped directly at ambient temperature of 20° to 30°C into a bath containing ingredients in the recommended proportions, with or without a solvent diluent, and agitated gently until the plated surface has been removed and base metal is uniformly exposed. The process may be speeded by raising the temperature of the bath to the boiling point but rapid NH₃ loss may occur. If temperatures approximating boiling are desired, equipment may be pressurized; but an operating temperature of from 50°C to 75°C gives rapid stripping with little loss of NH₃ from a properly manipulated system; i.e., simple covering of tanks is reasonably effective.

The system has greater selectivity than conventional solutions, and we have found that pH control may be of substantial help in the stripping operation and in improving the effectiveness of the removal of plated material. Since the system contains substantial concentrations of ammonia, metal ions are complexed with the use of excessively high pH’s and we have found we can conduct stripping operations under conditions which cannot be handled by other systems.

The rate of stripping nickel from the basis metal is determined by the rate of reaction with the nitrobenzene sulfonic acid compound. Actually, the mechanism of the operation of the bath seems to be one in which the nitrobenzene sulfonic acid dissolves the nickel in a direct stoichiometric reaction, but as the nickel passes into solution it becomes complexed with the ammonia therein and the excess ammonia keeps the pH of the solution at a high level to avoid attack on steel. Virtually any amount of the benzene sulfonic acid will strip metal and hence in defining the bath it is appropriate to say any concentration from 0 up to a maximum 1 molar ratio of the nitrobenzene sulfonate to 1 mol to 15 mols of the ammonia.

Since the ammonia functions as a complexing agent, it is best to maintain the concentration of the bath near an optimum high level of excess ammonia.

The bath will function to dissolve nickel regardless of the concentration of nitro benzene sulphate therein. Of course, for economical operation a reasonable rate of solution must be developed, so that the concentration of the bath is virtually a free variable, the only limitation being that the bath contain enough salts to carry out an effective amount of stripping.

Through use of the stripping system to remove plated metals from the base the aromatic acid components gradually become spent and the ammonia gradually becomes more and more nearly saturated with metal ions being held in complex form. It is feasible, however, to make additions of both the aromatic nitro compound, the ammonia compound, and the alkali to a partially spent bath so as to maintain a useful concentration of the free ammonia and the nitro compound oxidizing agent. Nickel may be removed via cathode exchange resin, precipitation, or electrolysis, and recombined.

The guide to the concentration of ingredients to be used is determined from the principles described. The concentration of the oxidizing agent may vary quite widely and is determined by the rate of solution needed for economic operation. It may be as low as 1 percent by weight in the solution, but preferably is about 5 to 10 percent. The concentration of the ammonia compound may be equivalent on a molar basis with that of the oxidizing agent to virtual saturation of the ammonia compound in the solution. The amount of caustic to be used is that needed to release ammonia and to fix pH in the range from about 7.5 to about 11.

The composition and use of a typical stripping bath is illustrated by the following examples wherein a stripping bath is prepared using blends of dry ingredients in accordance with the portions indicated.

Example 1

The following three compositions were tested and found to give good nickel stripping. The bath is not poisoned or inhibited by the presence of copper. Steel is not etched.

In preparing the baths it is convenient first to prepare the dry powder formulations, using parts by weight

<table>
<thead>
<tr>
<th>#1</th>
<th>#2</th>
<th>#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium nitrobenzenesulphonate</td>
<td>16.7</td>
<td>13.4</td>
</tr>
<tr>
<td>Ammonium sulphate</td>
<td>27.8</td>
<td>20.4</td>
</tr>
<tr>
<td>Sodium sulphate (30% Turns)</td>
<td>4.4</td>
<td>3.4</td>
</tr>
<tr>
<td>Urea</td>
<td>7.1</td>
<td>5.4</td>
</tr>
<tr>
<td>Wetting agent</td>
<td>5.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

1 E.O.: Vietvet (Vietor Chemical Co.)

These powders are mixed and can be preserved as the fundamental composition prior to actual use. The baths are operated in the following manner (example for 100 gallon tank).

The baths, corresponding to #1, 2, 3 are prepared as follows:

**Bath #1**—Suitable for room temperature operation, or for operation at elevated temperatures without additions.

Dry powder #1 163
Water 77
Ammonium hydroxide (29.6% aqueous) 100

Upon mixing, this bath is ready for operation.

**Bath #2**—Suitable for use where free ammonia addition is not desirable and especially where a bath is operated at 50° to 80°C, and an even rate of stripping is required over an eight hour day.

**Initial charge:**

Dry mixture #2 123
Sodium hydroxide (50%) 98
Water 92

Additions of dry mixture after 2, 4, and 6 hours of operation, each addition:

Dry mixture 27

**Bath #3**—Suitable for use at elevated temperature 50° to 80°C where an even rate of stripping is required over an eight hour day.

**Initial charge:**

Dry mixture #3 57
Ammonium hydroxide (29.4% aqueous) 35
Water 73.7

**Addition after 2 hours:**

Dry mixture 44
Ammonium hydroxide 35

**After 4 hours:**

Dry mixture 34
Ammonium hydroxide 35

**After 6 hours:**

Dry mixture 28
Ammonium hydroxide 35

In reporting these examples it is noted that the bath contains 100 gallons, more or less, and, as such, to require
replenishment, a full rate of use is assumed. The capacity of a bath of this concentration, at ambient temperature, is to dissolve about 1/2 ounce of metal per hour from a 2" x 2" metal coupon. To keep the rate of solution at this level, replenishment as indicated is made.

The sodium sulfide is added to the bath to provide sulfide ion, which inhibits the poisoning effect of copper. We have found that only small amounts of the sulfide ion should be used and actually relate the amount to preferred rates of stripping of the nickel. For example, the following bath was prepared:

<table>
<thead>
<tr>
<th>Sodium m-nitrobenzene sulphonate</th>
<th>grams</th>
<th>7.38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulphate</td>
<td>do</td>
<td>32.8</td>
</tr>
<tr>
<td>Urea</td>
<td>do</td>
<td>3.0</td>
</tr>
<tr>
<td>Ammonia</td>
<td>milliliters</td>
<td>30</td>
</tr>
<tr>
<td>Water</td>
<td>do</td>
<td>170</td>
</tr>
</tbody>
</table>

Tested with three concentrations of sodium sulfide the rate of nickel stripping, in the absence of copper, is greatly accelerated by the presence of a low concentration of S⁻ ions (e.g., as from Na₂S). Using 2" x 2" x 1/4" coupons of nickel in 220 milliliters of solution, at 80°C, the following data were attained:

<table>
<thead>
<tr>
<th>Number...</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Na₂S (60%)</td>
<td>0.00</td>
<td>0.63</td>
<td>1.00</td>
</tr>
<tr>
<td>Hours of stripping:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.45</td>
<td>2.58</td>
<td>1.92</td>
</tr>
<tr>
<td>2</td>
<td>0.34</td>
<td>0.97</td>
<td>1.04</td>
</tr>
<tr>
<td>3</td>
<td>0.31</td>
<td>0.29</td>
<td>0.82</td>
</tr>
<tr>
<td>4</td>
<td>0.28</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td>5</td>
<td>0.27</td>
<td>0.23</td>
<td>0.51</td>
</tr>
<tr>
<td>Total</td>
<td>1.66</td>
<td>4.77</td>
<td>4.14</td>
</tr>
<tr>
<td>Overall rate</td>
<td></td>
<td>3.1</td>
<td>4.7</td>
</tr>
</tbody>
</table>

The data show that with 1/4% of sodium sulfide in the medium, the rate stripping of nickel is increased by an overall factor of 3:1; with 1/2% of sodium sulfide, the rate is increased by a factor of only 2.7.

In the presence of copper, the rate of nickel stripping is inhibited. Sulfide ion, i.e., sodium sulfide, prevents this inhibition. The following fundamental bath was made up, with the variations noted in the table.

<table>
<thead>
<tr>
<th>Sodium m-nitrobenzene sulphonate</th>
<th>grams</th>
<th>7.38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulphate</td>
<td>do</td>
<td>32.8</td>
</tr>
<tr>
<td>Urea</td>
<td>do</td>
<td>3.0</td>
</tr>
<tr>
<td>Water</td>
<td>do</td>
<td>170</td>
</tr>
</tbody>
</table>

Loss of weight of 2" x 2" nickel coupon in grams in presence of 2" x 2" copper coupon commercial operation, we found that reduction by 15–30–45 percent, to a level about half the stated concentration, gave a rate of stripping directly proportional to the concentration of nitro-benzene sulphonate present. It is evident, therefore, that rate of stripping is proportional to the nitro-benzene sulphonates.

In summary, the composition of the bath may be described as follows:

**Dry Mixture**

<table>
<thead>
<tr>
<th>Preferred Weight</th>
<th>Useful Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na nitro-benzene sulphonate</td>
<td>13.4</td>
</tr>
<tr>
<td>Ammonium sulphate</td>
<td>81.8</td>
</tr>
<tr>
<td>(Sodium sulphide)</td>
<td>1.9</td>
</tr>
<tr>
<td>(Urea)</td>
<td>2.8</td>
</tr>
</tbody>
</table>

When bath is made up, add sodium hydroxide... | 24.0 | 10–40 |

In preparing the bath the user charges initially, for each 100 gallons of bath, for 25

<table>
<thead>
<tr>
<th>Dry mixture</th>
<th>lbs...</th>
<th>123</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydroxide (50%)</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>92</td>
<td></td>
</tr>
</tbody>
</table>

During use the operator adds 2, 4, and 6 hours, each, 30

| Dry mixture | lbs... | 27 |

The mechanism of this bath is that the strong sodium hydroxide base functions in the solution to release ammonia in quantity from the ammonium salt, thereby providing in solution the requisite nitro benzene sulphonate active ingredients in a medium containing an amount of ammonia suitable for complexing nickel.

In a bath of this type the molar ratio of constituents may vary widely with the optimum ratio being that which will exhaust the oxidizing agent which brings the nickel into solution and the ammonia complexing agent at approximately the same time.

The concentration of nitro compound-ammonia may vary widely. Effective removal of nickel is obtained with as little as 0.1 percent nitro compound in the presence of a high concentration of ammonia or with as much as a saturated solution of nitro compound in the presence of the lowest concentration of ammonia required to get the proper pH. The dilution of the active stripping composition may be as little as 1 percent of the nitro-compound-ammonia mixture in 99 percent of water or other solvent. The effectiveness of the extreme dilutions or ratios is low, but they are operative.

In place of the nitrobenzene sulphonate bath given in the above examples, the following nitro compounds may be used in corresponding stoichiometric amounts:

- (a) Di Nitroparaphene
- (b) Mixed isomers of nitrophthalic and isophthalic acids (commercial grade)
- (c) Nitrobenzene sulphonates, crude nitro benzoic acid mixture (ortho, meta, and/or para isomers)
- (d) o-, m-, p-Nitro-phenols; o-, m-, p-nitro anilines.

Generally any of the nitro organic compounds useful in cyanide stripping baths are useful in systems made in accordance with this invention with the advantage that pure single isomers need not be used. Thus, mixed o-, m-, p-isomers of the compounds given in United States Patents 2,649,361 and 2,698,781 may be used.

Observation of the solution may indicate that not all of the nitroaliphatic compound is in solution. As the stripping action progresses more of the nitro compound will go into solution, thereby maintaining a working concentration. Solvents may be used to put all components of the stripping composition in a single phase, and they do not necessarily improve efficiency.

Based on a variety of observations involved in stripping...
metal from several bases using compositions made in accordance with the invention in which the nature of the ammonia source was varied or with other sequestering agents in the bath, we have determined that the value of the stability constant of the metal complex formed by the stripped metal and ammonia compound in solution is a determining factor in identifying whether a given complexing agent is workable.

In recapitulation, the bath is characterized by several features, namely, its content of the nitro organic compound, with a trace of sulfur compound which yields sulfide ions, an ammonium salt, with an aqueous solution of ammonia. The solution should contain at least enough free ammonia to give a pH above about 7.5, preferably a pH of about 8.5. The free ammonia may be added to the solution as such or it may be formed in situ by reaction of caustic alkali with the ammonium salt. Under this set of conditions the solution is effective over a broad temperature range. Thus, the solutions specifically described in the examples are active for stripping at ambient temperatures; their activity at ambient temperature, i.e., 25-30°C, is about 80% of the activity at 80°C, when rate of stripping is used as the measure of activity.

In our copending applications, which may be considered fully incorporated herein, Serial No. 31,635,254, filed September 27, 1957, and Serial No. 789,772, now Patent No. 3,102,808, filed January 29, 1959, we have described, respectively, solutions for stripping and additives useful in such solutions, and this application may be considered a continuation-in-part thereof.

We have found that nickel, if desired, can be easily reclaimed from the stripping bath. In some cases this can be done by merely adding sulfide ions, which precipitate nickel sulfide. Such recovery practices are not practical when cyanide-based stripping baths are used. If desired the ammonia-nitro acid stripping bath may be acidified with concurrent release of metal ions which may then be plated from the solution by conventional electroplating procedures onto a sheet of nickel. This nickel sheet can then be used in the conventional nickel bath thus effecting essentially 100% recovery of the metal stripped. The nickel can also be absorbed directly from the ammonia complex with a cation exchange resin.

In general the stripping solution is used to reclaim a plated article, usually Ni, Co, Cd plate, because the value of the article substantially exceeds the cost of stripping. Hence, the solution will usually be in about the concentrations described in the examples. The variations, in the order of 0.01 to 1 percent of the active components, are useful when the mass of the article is small. For example, if it is necessary to strip nickel from an extremely fine gauge copper wire, the solution described in Example I, at neutral pH, and concentration of about 0.01 percent is useful. It removes the nickel rapidly enough to be economically useful, yet the conditions are such that the copper base, itself very small, is not affected.

Though the invention has been described in terms of a limited number of examples, it is to be understood that variants thereof may be practiced without departing from its spirit or scope.

What is claimed is:

1. An ammonia-yielding composition for selectively stripping nickel from a base metal in aqueous alkaline solution, characterized by its containing
   (1) a nitro substituted benzene compound and
   (2) an ammonia salt, (1) and (2) being present in major amount,
   (3) a sulfur compound in small amount, which sulfur compound yields at least a trace of sulfide ions in aqueous solution,
   said total composition being soluble in water,
   said composition when in aqueous solution together with a compound selected from the group consisting of ammonia and caustic alkali, being useful for stripping nickel from said base metal, the said total composition containing at least about 1 percent of said nitro benzene compound.

2. The composition of claim 1 in which the nitro compound corresponds to the formula RN02, wherein R is selected from the group consisting of benzene carboxylic acid moieties, benzene sulfonic acid moieties, benzene phosphonic acid moieties, and mixtures of the ortho, meta and para isomers of said acid moieties and said sulfonic, phosphonic and hydroxyl moieties and the alkali metal and ammonium salts thereof.

3. A composition in accordance with claim 1 useful for stripping a nickel coating from a base metal which comprises sodium meta nitrobenzenesulfonate, and ammonium sulfate, in a molar ratio of about 1 mol of nitro radical to about 15 mols of total ammonia.

4. A composition in accordance with claim 1 in which the sulfur compound is an alkali metal sulfide.

5. A composition in accordance with claim 2 which comprises about 2-20 parts of a nitro benzene sulfonate, about 10-80 parts of an ammonia salt and up to 1 part of alkali metal sulfide.

6. A composition in accordance with claim 5 in which the ammonia salt is ammonium sulfonate.

7. A composition in accordance with claim 3 which comprises about 16 parts of sodium nitrobenzenesulfonate, about 75 parts of ammonium sulfonate, and about 1 part by weight of sodium sulfide.

8. The method of stripping nickel from a base metal containing copper, on which said nickel has been deposited, which comprises providing a bath comprising about 60 parts by weight containing about 16 parts of sodium nitrobenzenesulfonate, 7.5 parts of ammonium sulfonate, as non-aqueous components and about 1 part by weight of sodium sulfide, and about 35 parts by weight of concentrated aqueous ammonia, dissolved in about 60 parts by weight of water,

maintaining said solution at a temperature in the range from room temperature to a level below about 80°C, substantially continuously stripping nickel from plated objects placed therein, and maintaining the level of nickel stripping activity of said solution over an extended period of about 8 hours by the successive steps of adding about 45 parts by weight of said nonaqueous components with 35 parts of hydroxide after about 2 hours, and adding about 34 parts by weight of ammonium hydroxide and 34 parts by weight of nonaqueous components after about 4 hours, and adding about 28 parts of nonaqueous components and 35 parts of ammonium hydroxide after about 6 hours, whereby the stripping capacity of said solution is maintained at a substantially optimum level approximating starting activity over a period of at least 8 hours.

9. A composition for stripping nickel from a base on which it has been electrodeposited which comprises about 7 parts by weight of sodium nitrobenzenesulfonate, about 32 parts by weight of ammonium sulfonate, about 35 parts by weight of concentrated aqueous ammonium hydroxide, said materials when dissolved in about 170 parts by weight of water, forming a solution for stripping nickel, the said solution being further characterized by the presence of less than about 1% of sulfide ions.

10. A composition suitable for stripping nickel from a metal base on which it has been deposited which comprises about 2-20 parts by weight of sodium nitrobenzenesulfonate, about 10-80 parts by weight of ammonium sulfonate, and less than one part by weight of sodium sulfide, said components when dissolved in water
with about 10–40 parts by weight of sodium hydroxide constituting a suitable solution for stripping electrodeposited nickel from an electrodeposited copper base.

11. A composition in accordance with claim 10 consisting essentially of about 13 parts by weight of sodium nitrobenzene sulphonate, about 80 parts by weight of ammonium sulphate, about 1 part by weight of sodium sulfide, and about 24 parts by weight of sodium hydroxide, said components being soluble in water to give a solution suitable for stripping nickel from a metal base.


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RAY K. WINDHAM, BENJAMIN HENKIN, Examiners.