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STRESS CORROSION CRACKING IN AMMONIA PLANTS[1/]

by

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INTRODUCTION

Stress corrosion cracking (S C C) may be defined as a non-ductile fracture resulting from the simultaneous application of a tensile stress and a specific corrodent. A lot of laboratory time is spent on research into the mechanism of S C C but no unified theory has as yet emerged and it is not proposed to enter into a discussion of rival theories. Good reviews have been published (1, 2). The function of corrosion engineering is to minimize the effects of stress corrosion on plant equipment with respect to both consequential hazards and plant profitability. The obvious method is to avoid completely those materials of construction which are susceptible under operating conditions. In most cases an alternative material can be chosen but this frequently involves a cost penalty. Methods of using susceptible materials in a safe manner are an attractive alternative but require a knowledge of all the factors affecting the phenomenon. The factors of greatest importance to the Corrosion Engineer may be stated:-

1. The corrodent is specific for individual metals and alloys. Table I is a partial list of the more common S C C situations. The fact that a reagent attacks a metal does not necessarily mean that stress cracking will result. In fact the specific stress corrosion reagent is frequently one in which immeasurably small metal loss would occur by uniform corrosion in the period to failure.

2. The application of stress and corrodent must be simultaneous. Alternate exposure to stress and corrosion can induce failure but it will not be a stress corrosion failure.

3. The stress does not have to result from an applied load. Residual stresses in deformed material are frequent causes of failure. The stress level necessary to cause S C C varies from one system to another. In, for example, the nitrate cracking of carbon steel stresses near to yield are necessary. moderate elastic stresses failing to induce S C C even over extended exposures whereas the limit below which no S C C can occur in the ammonia/brass system is a fraction of the yield stress.

4. A factor of overriding importance is the concentration of a specific ion in the layer of liquid in contact with the metal. It is important to distinguish this from the bulk concentration. There are many circumstances in which stress corrosion has occurred only in those places where some physical factor has caused the specific ion to concentrate locally. A typical example is the splash zone in a jacketed vessel. Liquid splashed onto the wall above the water line evaporates to give a concentrated solution which produces S C C even when the metal exposed to the bulk liquid shows no such failure.

5. Increase in temperature promotes stress corrosion cracking. In some systems there is a limiting temperature below which the time to initiation is so long that for all practical purposes the system can be considered immune. In others, for example brass in ammonia solutions cracking occurs readily at ambient temperature.

6. There is a time lag between exposure to S C C conditions and the initiation of a detectable crack, the so-called induction period. In any given system the delay is a complex function of stress level, corrodent concentration, temperature etc. Even when all the factors are fully and precisely known the time to initiation of a crack can be predicted only on a statistical basis. Each individual crack initiation is a random event.

7. Crack propagation is rapid although orders of magnitude slower than a brittle facture. It is rare for cracking to be continuous, more frequently it occurs in a series of steps and the time to ultimate failure may be prolonged, up to years in some instances.

8. Cracking is normally perpendicular to the applied stress but is frequently irregular in direction, following microstresses imposed by inhomogenities in the metal. S C C is frequently characterised by multiple branching. The form similar to a river delta shown in Plate I is usually referred to as a 'typical stress corrosion crack'.

While this crack morphology is common it is not exclusive. Plate 2 is a photomicrograph of another crack in the same specimen as Plate I. In this case the branches are short, show no secondary branching and are orthogonal to the main crack axis, but both plates illustrate transgranular chloride stress corrosion cracking in austenitic stainless steel. Plate 3 illustrates ammonia stress cracking of brass. Again the morphology is different, the cracks are exclusively intergranular. In some cases mixed, ie both intergranular and transgranular paths are seen in the same crack. In some two phase alloys it is not uncommon to find a fracture which is propagated as a stress corrosion crack in one phase and as a cleavage crack in the other.

IMPLICATIONS OF S.C.C. IN PRACTICE

The importance that corrosion engineers attach to S.C.C. may be measured by the number of papers devoted to the subject published in corrosion engineering journals. It would be unwise to assume that this is a true reflection of either the hazards or the cost of the phenomenon. There are some features of S.C.C. that increase its importance to plant operators beyond that associated with safety or process economics. The progress of most forms of corrosion can be predicted with a reasonable precision, sufficient for remedial action to be planned. There may, for example, be circumstances in which it is necessar to employ a material which corrodes at such a rate that failure will occur in say three years. It is possible to live with this situation by preventative maintenance ie, by replacing the item at two year intervals. With S.C.C. on the other hand such preventative measures are ineffective. Replacing an item prior to failure gives no guarantee that the replacement will be any more reliable than the original. Hence the effort expended on understanding S.C.C. in order to avoid completely the situations in which it occurs.

The hazards associated with S.C.C. can be exagerated. It is rare for stress corrosion to give rise to a catastrophic failure, a leak of moderate dimensions is the usual outcome. However catastrophic failures are not unknown and even a small leak can be hazardous if the contained fluid is inflammable or toxic.

A stress corrosion crack can form an acute notch at which corrosion fatigue can initiate. This is a real hazard in moving machinery eg fans, and in items subject to cylical stresses, eg. pulsation dampers.

GENERAL STRESS CORROSION FAILURES IN AMMONIA PLANTS

Neglecting the main process fluids, ammonia plants share a number of corrosion environments with other types of process plant. All equipment is exposed to atmosphere with moisture and the usual pollutants. The majority of plants use cooling water and many raise steam from process heat and treated boiler water and collect steam condensate. It is in this area rather than the one specific to process liquors that the majority of stress corrosion failures occur. I intend to describe three metal/stress corrodent systems that have given rise to failure on ammonia plants.

AMMONIA STRESS CORROSION OF BRASS

All copper alloys are attacked to some extent by aqueous ammonia solutions. The brasses, copper/zinc alloys containing more than 20% zinc, suffer rapid stress corrosion cracking in solutions and moist atmospheres containing no more than a few ppm of ammonia. The cracking is usually intergranular, it can occur at ambient temperatures and requires only moderate elastic stresses. The suceptibility is not significantly affected by alloying additions eg admiralty brass (2% tin) aluminium brass (2% aluminium), silicon brass (up to 4% Si), white brass (nickel silver, up to 15% Nickel) are all susceptible. Alloys containing a lower zinc content, gunmetal, gilding metal (15% Zn) are not immune but they are so much more resistant that it is rare for the risk of stress corrosion to need consideration in engineering design.

Among the zinc free copper alloys, the cupronickels are substantially immune. The tin bronzes are suceptible to high concentrations only in the heavily cold worked condition. Pure copper is sometimes said to be immune but cases of cracking of OFHC copper have been reported and certainly PDO copper used for tubing can be cracked in the fully hard drawn condition. The aluminium and silicon bronzes are relatively resistant to ammonia but have their own specific S C C corrodents. Time to failure at a given stress level is a function of ammonia ion concentration, and pH and the presence of oxidising agents usually dissolved oxygen. Under moderately aggresive conditions protection can be afforded by inhibitors which form copper complexes more stable than the cuprammonium complex eg. Benzoltriazole or substituted dithio carbamates,

One of the first recorded cases of stress corrosion of brass originated in India when the British Army noted cracking of brass cartridge cases stored under poor conditions during the monsoon season, hence the common name for the phenomenon - Season Cracking. High temperature and humidity caused emission of ammonia by the decomposition of one of the constituents of the smokeless powder, and temperature cycling in poor storage conditions permitted condensation of ammonia contaminated moisture on the brass, already highly stressed by the cold drawing operation used in manufacture.

There is always a risk of ammonia contamination of atmosphere and cooling water on an ammonia plant and no one deliberately employs brass in such an environment. Many items of equipment however are not subject to detailed specification by the plant designer but are purchased "off-the-shelf" as part of a package deal. Typically, the oil coolers of a machine are part of the machine vendors packet and unless great care is taken they are apt to be supplied with brass tubes and tube sheets. Oil systems are frequently common to turbines and compressors and can be contaminated with ammonia and water hence there is a risk of cracking being initiated on the oil side. Recirculated cooling water supplies can be contaminated with ammonia from process leaks and hence the water side of the coolers is also at risk. The risk from the oil side can be minimised by the addition of an inhibitor to the oil, benzoltriazole is usually used, but specific copper inhibitors in the cooling water are of doubtful economic value. The lubrication of major machines on an ammonia plant is of such critical importance for long term trouble-free operation that the extra initial expense of cupronickel oil coolers is justified.

Fittings for instrument air lines are commonly made as hot pressings in 60:40 duplex brass. Alternatives are available, gunmetal castings for example, but they are non-standard items and difficult to procure. Hence many ammonia plants have copper instrument air and steam tracing tubes connected by brass fittings which can fail by the action of ammonia contaminated atmospheric mois

Failure rarely constitutes a hazard but can upset plant operation. Some protection can be given to brass fittings by wrapping with lanoline impregnated tape. The protection is improved, if prior to wrapping, the brass is painted with a solution of benzoltriazole in IPA to leave a deposit of inhibitor on the surface.

It may be a useful illustration to record an incident on an ammonia plant involving a Bourdon pressure gauge. The gauge was intended for ammonia duty as it was calibrated in psi Ammonia and bore the legend "Bored Steel Tube". Three days after installation the glass fell out, two days later it ceased to register. Investigation showed the glass was held in place by a spun brass bezel and the internal mechanism included white brass gears and a phosphor bronze hair spring. All these items had failed by stress corrosion induced by ammonia contaminated atmospheric moisture.

CHLORIDE STRESS CORROSION OF AUSTENITIC STAINLESS STEEL

Austenitic stainless steel is subject to stress corrosion in solutions containing chloride ions. Crack initiation is very temperature dependent, below 70°C cracking is so rare as to require no consideration, between 70 and 100°C very high local concentrations of chloride ions are necessary and the induction period is prolonged. Only at temperatures above 100°C does cracking occur in moderate chloride ion concentrations. Cooling water inevitably contains some chloride but it is rare for the concentration to be more than 1000 ppm. Stainless steel should be safe in such solutions unless the design and process operation is such as to give rise to a situation in which concentration can occur. Unfortunately unless great care is taken such situations are common. A typical example is the normal tubular heat exchanger. If the cooling water is on the shell side and the process side temperature is high, water in the tube/tubeplate crevices will boil causing high concentrations of chloride ions within the crevice and failure of the tubes. If the cooling water is in the tubes and they become fouled by porous deposits from the water, heat transfer will be restricted, the metal wall temperature will rise and evaporation of water will occur in the pores of the deposit again leading to sufficiently high local chloride concentrations to initiate cracking. No efficient chloride stress corrosion inhibitor is available for addition to the water even if it were economic to do so.

Stress relief of complete items has also proved ineffective. Handling and operating stresses are sufficiently high to permit S.C.C. The only method of prevention therefore is a complete avoidance of the particular situation. A general rule that austenitic stainless steel should not be used for coolers with water on the shell side at process temperatures exceeding 70°C or with water on the tube side at process temperatures exceeding 100°C is probably conservative but has been shown to eliminate risk of failure for all practical purposes. If these temperatures have to be exceeded alternative materials must be selected. Previously this involved the use of expensive high nickel alloys such as incolloy 825 but considerable satisfactory experience has now been obtained on the so called austenitic/ferritic stainless steels which while not entirely immune to chloride cracking show sufficiently high resistance to make them economically attractive.

Another very common cause of stress corrosion cracking of stainless steel equipment is the concentration of rain water containing traces of chlorides on the surface of equipment under lagging. If lagging is applied to a hot stainless steel vessel and is not completely sealed against the ingress of rain water, plant leakages, wash water etc there will be a gradual build up of chloride ions at a position within the lagging where the water evaporates. When the metal temperature falls during eg a shutdown, this high chloride front will move inwards to contact the metal wall. When the temperature rises again the metal surface will be in contact with a solution rich in chlorides and cracking may result. The obvious method of avoidance is to ensure that water does not enter the lagging by efficient weather proofing. It is difficult to guarantee this throughout the life of a plant, and therefore further precaustions are necessary. The use of an aluminium foil wrapper between the stainless steel and the lagging has proved efficient in service. The aluminium foil serves two functions. It acts as an isothermal barrier between the equipment and the lagging, ensuring that any water that penetrates will evaporate before it reaches the stainless steel. If the lagging becomes accidently flooded with water so that liquid fills the crevices between the aluminium and the stainless steel then the aluminium will corrode and in so doing will provide cathodic protection to the stainless steel.

CAUSTIC CRACKING OF CARBON STEEL

Years ago when boilers were of rivetted construction and were fed with boiler feed water made alkaline with caustic alkalies, stress corrosion cracking was a common cause of failure. It usually resulted from operation with a minor leak around a rivet leading to evaporation and local high concentrations of caustic alkalies. The high pressure boilers on a modern ammonia plant could not operate under these conditions and such failures are probably a thing of the past. However slight maloperation of the boiler feed water dosing equipment can give rise to traces of caustic alkalinity in the boiler drum and I have investigated one incident in which this caused caustic cracking of a blown-down pipe at a point beyond the blowdown valve where flashing-off occurred.

Ammonia plants sometimes have to handle caustic soda solutions for cooling water treatment and resin regeneration in demineralisation plants. These solutions are frequently 40-45% strength and equipment is steam heated to prevent freezing. Caustic cracking can occur if the metal wall temperature exceeds 80°C. This is not uncommon if, for example, the steam is left on after flow of the solution of caustic has stopped. Caustic cracking requires stress level close to the yield point and if all equipment exposed to steam and caustic is stress relieved there should be no risk of failure.

STRESS CORROSION PECULIAR TO AMMONIA PLANTS

CO_2 REMOVAL SYSTEMS

One of the more common systems of CO_2 removal used on ammonia plants is the so-called Vetrocoke system which employs a solution of arsenious oxide in potassium carbonate solution. The arsenic serves a dual purpose acting as an activator improving the efficiency of CO_2 removal and as an inhibitor preventing the corrosion of mild steel which would otherwise occur in the potassium carbonate/bicarbonate solution resulting from the absorption of carbon dioxide. Although some of these plants have been in operation for many years it was not until about 1968 that it became clear that this solution was a specific stress corrodant for carbon steel. ICI carried out an exhaustive investigation both in the laboratory and by collecting reported failures world-wide. The following facts emerged from the laboratory work:

1. The mechanism of inhibition by arsenic was a shift in the free corrosion potential of carbon steel in a more positive direction. In the absence

of arsenic, the free corrosion potential lay in the active region. In the presence of arsenic it lay on the borderline between active and passive.

2. Stress corrosion occurred only when the metal was at the active/passive transition.

3. The free corrosion potential could be shifted fully into the passive region by the addition to the solution of a small concentration of antimony ions and a ferric ions and a solution so treated did not stress corrode. (ref 3).

These results explained some observations which were made as a result of the analysis of plant failures.

a) Not all plants suffered stress corrosion. Those that escaped were ones employing arsenic from a source which contained a proportion of antimony as a natural impurity.

b) Among the plants which suffered were a few which used impure arsenic containing antimony but which did not employ air-sparging and in which therefore any iron ions would be present as ferrous rather than ferric ion.

As a result of this investigation ICI devized a system of adding antimony, monitoring the free corrosion potential of the plant by installing a specially designed reference electrode and sparging with air to maintain the measured potential above predetermined limits. This system is the basis of patents and patent application (ref 3) and is available on license and has been installed successfully on seven plants. A detailed account of the investigation has been published (ref 4). This work led to a more exhaustive investigation into the mechanism of inhibition by redox potential systems such as AS^{5+}/As^{3+}, V^{5+}/V^{4+} etc and a safe biodegradable inhibitor has been discovered which could be used as a substitute for vanadium in other CO_2 removal systems (ref 5).

CARBON STEEL IN LIQUID AMMONIA

Liquid ammonia is an ionizing solvent like water and solutions in liquid ammonia can produce corrosion phenomena similar to those more usually experienced in aqueous solutions.

A number of accidents have occurred as a result of stress corrosion of quench tempered steels in impure liquid ammonia. Research by Phelps (ref 6) showed that the active agent was oxygen dissolved in liquid ammonia and that the stress corrosion reaction could be inhibited by the addition of water. It was later found that cracking was not confined to high strength steels but could occur with ordinary carbon steels. Although no serious occurrences have been reported, investigations throughout Europe have shown extensive cracking in a number of Horton spheres used to store liquid ammonia under pressure at near ambient temperatures. A number of firms have jointly sponsored research into the problem. The results so far available show that cracking does not occur below about 10 ppm dissolved oxygen and above this the reaction is inhibited by water additions. The results have implications for ammonia producers. It is unlikely that plant equip ent will ever be in contact with ammonia containing sufficient oxygen to be dangerous but storage and transport of liquid ammonia must be such as to ensure against the ingress of air or alternatively there must be the deliberate addition of sufficient water to inhibit stress corrosion.

STRESS CORROSION PREVENTION

A survey carried out in the States in 1961-62 showed that 39% of the corrosion failures of chemical plant equipment were due to stress corrosion. A similar analysis of the corrosion failures investigated in the Teesside Materials Group corrosion laboratories of ICI for 1973-74 showed only 8% as being stress corrosion failures. The difference, in my opinion, may be ascribed to the increasing awareness of the problem and the improved precautions taken over the 10 years but it must be emphasized that this improvement has been obtained only at a cost. The methods of preventing stress corrosion and the cost penalties may be summarized.

1. Improved materials selection. Where the traditional material of construction is known to be subject to the risk of SCC an alternative may be chosen. The alternative is usually more expensive, frequently very much more. This increases capital costs not only in purchase of material but in time of procurement and delays and expense in fabrication in a material to which the manufacturer is not accustomed.

2. Stress relief. This again involves capital cost and sometimes delay in completion.

3. Improved design. Frequently all that is necessary is a change in detailed design of equipment, for example, the elimination of crevices in a jacketed reactor. However an exhaustive study of the design and operation of the equipment has to be undertaken by process designers, mechanical designers and materials specialists working together as a team, if all risks are to be eliminated and such design effort is expensive and time consuming.

4. Process limitation. If all other methods are inapplicable it may be necessary to limit plant operation, either in terms of operating temperatures or sources of feedstocks etc. in order to prevent the equipment being exposed to the risk. This can result in operation below maximum efficiency and carries an economic penalty in terms of reduced revenues.

It is probable that stress corrosion failures will never be completely eliminated. New processes and new materials are likely to involve stress corrosion situations which cannot be predicted on existing knowledge. The known stress corrosion failures could be prevented but only at a cost of time, money and skilled effort.

References

1. The Theory of Stress Corrosion Cracking in Alloys. Ed J C Scully North Atlantic Treaty Organisation. Scientific Affairs Division. Brussels 1971.

2. Fundamental Aspects of Stress Corrosion Cracking Proceedings of Conference Ohio State University September 1967

3. British Patent Application 22356/73
South African Patent No 2508/74

4. D Fyfe Safety in Air and Ammonia Plants Conference 1973

5. British Patent Application 44408/74

6. E H Phelps Ammonia Plant Safety 16, 32 1974

Table 1

STRESS CORROSION CRACKING SYSTEM

Alloy	Corrodent
Carbon Steel	Hydroxyl ions Nitrate ions Caronate/Bicarbonate ions
Austenitic Stainless Steel	Chloride ions Hydroxyl ions Polythionic acid
Nickel Alloys	Hydroxyl ions
Copper Alloys	Ammonium ions Sulphite ions
Aluminium Alloys	Water and salts
Titanium	Red fuming nitric acid Anhydrous methanol

PLATE I BRANCHING STRESS CORROSION CRACK IN AUSTENITIC STAINLESS STEEL

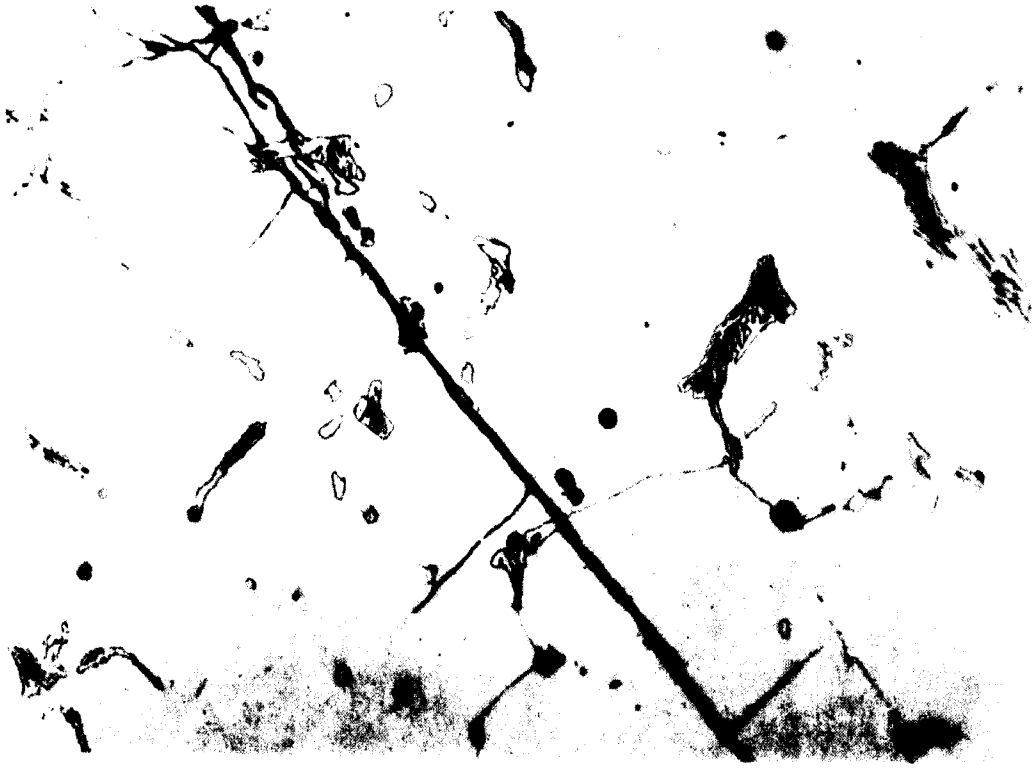

PLATE 3 INTERGRANULAR STRESS CORROSION CRACKS IN BRASS

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STRESS CORROSION CRACKING IN AMMONIA PLANTS[1/]

SUMMARY

by

Mervyn E.D. Turner*

The causes, nature and effects of stress corrosion cracking are described. The approach is a corrosion-engineering one being concerned with the practical effects of engineering design and process operation on the risk of failure rather than a study of the mechanisms involved.

The unique relationship between an alloy and a specific stress corrosion agent is emphasised by a partial list of the common systems in which stress corrosion has been observed.

Ammonia plants share with a number of other process plants environments in which stress corrosion of common alloys can occur. Three of these are chosen for discussion. They comprise the 'season cracking' of brass, the caustic cracking of carbon steels and the chloride cracking of austenitic stainless steels. In each case the influence of ion concentrations in the corrosion and alloy composition in the metal are discussed. Practical steps to eliminate the risk of failure are described.

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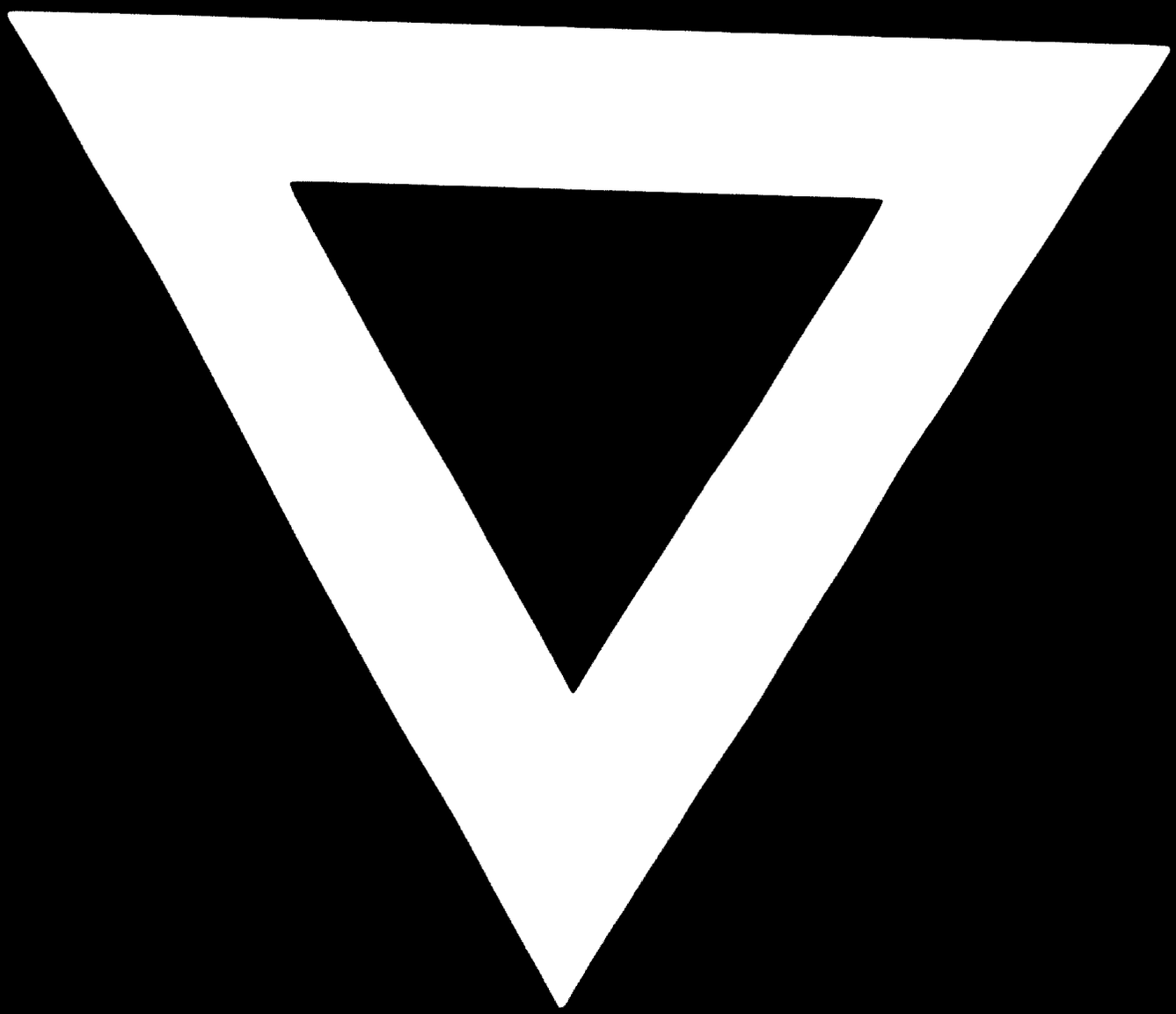

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