SAFETY DATA SHEET

PRODUCT NAME: AMMONIUM BIFLUORIDE

Issue Date: April 23

IDENTIFICATION

Product Name: Ammonium Bifluoride
Other Names: Ammonium hydrogen fluoride; Ammonium acid fluoride; Ammonium difluoride; Ammonium hydrogen difluoride; Ammonium bifluoride; Ammonium hydrofluoride.
Product Code: ZABIFL
Uses: In manufacture of magnesium and magnesium alloys; in brightening of aluminum; for purifying and cleansing various parts of beer-dispensing apparatus, tubes, etc. sterilizing dairy and other equipment. In glass and porcelain industries; as mordant for aluminum; as a 'sour' in laundering cloth. In the laboratory production of hydrogen fluoride.
Supplier: HamChem Hamilton Chemicals Ltd, 75 Ruffell Rd, Hamilton
Phone: 07 974 4971 Web: www.hamchem.nz Email: info@hamchem.nz

- **In emergency dial 111, and then ask for Fire, Ambulance or Police as necessary.**
- **In case of poisoning phone National Poisons Centre – 0800 764 766**

HAZARD IDENTIFICATION

GHS Classifications
Acute Oral Toxicity – Category 3
Skin Corrosion – Category 1C
Serious Eye Damage – Category 1

Signal Word: DANGER

Hazard Statements
H301 Toxic if swallowed
H314 Causes severe skin burns and eye damage
H318 Causes serious eye damage

Precautionary Statements

Prevention
P264 Wash hands thoroughly after handling
P260 Do not breathe dusts or mists
P270 Do not eat, drink or smoke when using this product
P280 Wear protective gloves/protective clothing/eye protection/face protection

Response
P301+P310 - IF SWALLOWED: Immediately call a POISON CENTRE or Doctor/Physician
P330 Rinse mouth
P301+P330+P331 – IF SWALLOWED: Rinse mouth. Do NOT induce vomiting

P303+P361+P353 IF ON SKIN (or hair): Remove/take off immediately all contaminated clothing. Rinse skin with water/shower.
P363 Wash contaminated clothing before reuse
P304+P340 IF INHALED: Remove person to fresh air and keep comfortable for breathing.
P310 Immediately call a POISON CENTRE or Doctor
P305+P351+P338 – IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do so. Continue rinsing.
P310 Immediately call a POISON CENTRE or Doctor

Storage
P405 – Store locked up

Disposal
P501 – Dispose of contents/container in accordance with local regulations

COMPOSITION & INFORMATION ON INGREDIENTS

Chemical Entity	CAS No.	Proportion (%)
Ammonium Bifluoride	1341-49-7	≥ 98
Impurities may include:		
Ammonium Fluoride	12125-01-8	<2%
Hydrogen Fluoride	7664-39-3	<0.01%
Ammonium Fluorosilicate	16919-19-0	<0.05%

FIRST AID MEASURES

Inhalation: If dust is inhaled, remove from contaminated area. Encourage patient to blow nose to ensure clear breathing passages. Ask patient to rinse mouth with water but to not drink water. Seek immediate medical attention. For massive exposures – if dusts, vapours, aerosols, fumes or combustion products are inhaled, remove from contaminated area. Lay patient down. Keep warm and rested. Prostheses such as false teeth, which may block airway, should be removed, where possible, prior to initiating first aid procedures. Apply artificial respiration if not breathing, preferably with a demand valve respirator, bag-valve mask device, or pocket mask as trained. Perform CPR if necessary. If victim is conscious, give six **calcium gluconate or calcium carbonate tablets** in water by mouth. Transport to hospital, or Doctor URGENTLY.

Skin Contact: If there is evidence of severe skin irritation or skin burns: Avoid further contact. Immediately remove contaminated clothing, including footwear. Flush skin under running water for 15 minutes. Avoiding contamination of the hands, massage **calcium gluconate gel** into affected areas, pay particular attention to creases in the skin. Contact the Poisons Information Centre. Continue gel application for at least 15 minutes after burning sensation ceases. If pain recurs, repeat application of calcium gluconate gel or apply every 20 minutes. If no gel is available, continue washing for at least 15 minutes, using soap if available. If patient is conscious, give six **calcium gluconate or calcium carbonate tablets** in water by mouth. Transport to hospital, or Doctor URGENTLY.

Eye Contact: If this product comes into contact with the eyes: immediately hold eyelids apart and flush the eye continuously with running water. Ensure complete irrigation of the eye by keeping eyelids apart and away from the eye and moving the eyelids occasionally by lifting the upper and lower lids. Continue flushing until advised to stop by the National Poisons Centre or a Doctor, or for at least 15 minutes. Transport to hospital or Doctor without delay. Removal of contact lenses after an eye injury should only be undertaken by skilled personnel.

Ingestion: For advice, contact National Poisons Centre or a Doctor at once. Urgent hospital treatment is likely to be needed. If swallowed, do NOT induce vomiting. If vomiting occurs, lean patient forward or place on left hand side (head down position, if possible) to maintain open airway and prevent aspiration. Observe the patient carefully. Never give liquid to a person showing signs of being sleepy or with reduced

awareness; i.e., becoming unconscious. Give water to rinse out mouth, then provide liquid slowly and as much as casualty can comfortably drink. Transport to hospital or Doctor, without delay.

Indication of any immediate medical attention and special treatment needed

For acute or short-term repeated exposures to fluorides: Fluoride absorption from gastro-intestinal tract may be retarded by calcium salts, milk or antacids. Fluoride particulates or fume may be absorbed through the respiratory tract with 20-30% deposited at alveolar level. Peak serum levels are reached 30 mins. Post-exposure; 50% appears in the urine within 24 hours. For acute poisoning (endotracheal intubation if inadequate tidal volume), monitor breathing and evaluate/monitor blood pressure and pulse frequently since shock may supervene without warning. Monitor ECG immediately; watch for arrhythmias and evidence of Q-T prolongation or T-wave changes. Maintain monitor. Treat shock vigorously with isotonic saline (in 5% glucose) to restore blood volume and enhance renal excretion. Where evidence of hypocalcaemic or normocalcaemic tetany exists, calcium gluconate (10ml of 10% solution) is injected to avoid tachycardia.

For acute or short-term repeated exposures to strong acids: Airway problems may arise from laryngeal edema and inhalation exposure. Treat with 100% oxygen initially. Respiratory distress may require cricothyroidotomy if endotracheal intubation is contraindicated by excessive swelling. Intravenous lines should be established immediately in all cases where there is evidence of circulatory compromise. Strong acids produce a coagulation necrosis characterized by formation of a coagulum (eschar) as a result of the desiccating action of the acid on proteins in specific tissues.

INGESTION: Immediate dilution (milk or water) within 30 minutes post ingestion is recommended. DO NOT ATTEMPT TO NEUTRALISE THE ACID SINCE EXOTHERMIC REACTION MAY EXTEND THE CORROSIVE INJURY. Be careful to avoid further vomit since re-exposure of the mucosa to the acid is harmful. Limit fluids to one or two glasses in an adult. Charcoal has no place in acid management. Some authors suggest the use of lavage within 1 hour of ingestion.

SKIN: Skin lesions require copious saline irrigation. Treat chemical burns as thermal burns with non-adherent gauze and wrapping. Deep second-degree burns may benefit from topical silver sulfadiazine.

EYE: Eye injuries require retraction of the eyelids to ensure thorough irrigation of the conjunctival cul-de-sacs. Irrigation should last at least 20-30 minutes. DO NOT use neutralizing agents or any other additives. Several litres of saline are required. Cycloplegic drops (1% cyclopentolate for short-term use or 5% homatropine for longer term use) antibiotic drops, vasoconstrictive agents or artificial tears may be indicated dependent on the severity of the injury. Steroid eye drops should only be administered with the approval of a consulting opthamologist.

FIRE FIGHTING MEASURES

Extinguishing Media: Water spray or fog, foam, dry chemical powder, BCF (where regulations permit).

Fire Incompatibility: None known.

Fire-Fighting: Alert Fire Brigade and tell them location and nature of hazard. Wear full body protective clothing with breathing apparatus. Prevent, by any means available, spillage from entering drains or water course. Use fire-fighting procedures suitable for surrounding area.

Fire/Explosion Hazard: Noncombustible. Not considered to be a significant fire risk. Acids may react with metals to produce hydrogen, a highly flammable and explosive gas. Heating may cause expansion or decomposition leading to violent rupture of containers.

Products of Decomposition: Decomposition may produce toxic fumes of Hydrogen Fluoride & Nitrogen Oxides.

ACCIDENTAL RELEASE MEASURES

Minor Spills: Remove all ignition sources. Clean up all spills immediately. Avoid contact with skin and eyes. Control personal contact with the substance by using protective equipment. Drains for storage or use areas should have retention basins for pH adjustments and dilution of spills before discharge or disposal of material. Check regularly for spills and leaks.

Major Spills: Clear area of personnel and move upwind. Alert Fire Brigade and tell them of location and nature of hazard. Wear full body protective clothing with breathing apparatus. Prevent, by any means available, spillage from entering drains or water course.

HANDLING & STORAGE

Safe Handling: Avoid all personal contact, including inhalation. Wear protective clothing when risk of exposure occurs. Use in a well-ventilated area. Warning: to avoid violent reaction, ALWAYS add material to water and NEVER water to material. Store in original containers, keep containers securely sealed. Store in a cool, dry, well-ventilated area. Store away from incompatible materials and foodstuff containers.

Suitable Container: Do NOT use aluminum or galvanized containers. Check regularly for spills and leaks. Do NOT use unlined containers. Use lined metal can, lined metal pails/can, plastic pail, polyliner drum, packaging as recommended by manufacturer. For low viscosity materials – drums and jerricans must be of the non-removable head type. Where a can is to be used as an inner package, the can must have a screwed enclosure. For materials with a viscosity of at least 2680 cSt. (23°C) and solids (between 15°C and 40°C) – removable head packaging, cans with friction closures and low-pressure tubes and cartridges may be used. Material is corrosive to most metals, glass and other siliceous materials.

Storage Incompatibility: Salts of inorganic fluoride: react with water forming acidic solutions, are violent reactive with boron, bromine pentafluoride, bromine trifluoride, calcium disilicide, calcium hydride, oxygen difluoride, platinum, potassium. In aqueous solutions are incompatible with sulphuric acid, alkalis, ammonia, aliphatic amines, alkanolamines, alkylene oxides, amides, epichlorohydrin, isocyanates, nitromethane, organic anhydrides, vinyl acetate. Corrodes metals in presence of moisture. May be incompatible with glass and porcelain. Ammonium bifluoride: reacts with water forming a weak solution of hydrofluoric acid. Reacts violently with bases ammonia gas. Attacks glass, cement and most metals in the presence of moisture. Upon contact with moisture and metal, may release flammable hydrogen gas which can collect in confined spaces – avoid aluminum, nickel or steel containers. When heated to decomposition emits toxic and corrosive fumes of ammonia, hydrogen fluoride and nitric oxides. Inorganic acids are generally soluble in water with the release of hydrogen ions. The resulting solutions have pH's of less than 7.0. Inorganic acids neutralize chemical bases (for example: amines and inorganic hydroxides) to form salts – neutralization can generate dangerously large amounts of heat in small spaces. The dissolution of inorganic acids in water or the dilution of their concentrated solutions with additional water may generate significant heat. Contact with acids produces toxic fumes.

EXPOSURE CONTROLS & PERSONAL PROTECTION

Exposure standards:
New Zealand Workplace Exposure Standards have been set by WorkSafe NZ

Ingredient	Material Name	TWA	STEL	Peak	Notes
Ammonium bifluoride	Fluorides, as F	2.5mg/m³	Not available	Not available	(bio) – exposure can also be estimated by biological monitoring.
Ammonium fluoride	Fluorides, as F	2.5mg/m³	Not available		bio) – exposure can also be estimated by biological monitoring.

Ingredient	Material Name	TWA	STEL	Peak	Notes
Hydrogen Fluoride	Hydrogen Fluoride, as F	Not available	Not available	2.6mg/m³ 3ppm	Not available
Ammonium fluorosilicate	Fluorides, as F	2.5mg/m³	Not available		bio) – exposure can also be estimated by biological monitoring.

Emergency Limits:

Ingredient	Material Name	TEEL-1	TEEL-2	TEEL-3
Ammonium bifluoride	Ammonium hydrogen fluoride	11mg/m³	130mg/m³	750mg/m³
Ammonium Fluoride	Ammonium Fluoride	15mg/m³	160mg/m³	980mg/m³
Hydrogen fluoride	Hydrogen Fluoride (hydrofluoric acid)	Not available	Not available	Not available
Ammonium fluorosilicate	Ammonium hexafluorosilicate (ammonium silicofluoride)	12mg/m³	130mg/m³	780mg/m³

Appropriate Engineering Controls: Engineering controls are used to remove a hazard or place a barrier between the worker and the hazard. Well-designed engineering controls can be highly effective in protecting workers and will typically be independent of work interactions to provide this high level of protection. The basic types of engineering controls are: Process controls which involve changing the way a job activity or process is done to reduce the risk. Enclosure and/or isolation of emission source which keeps selected hazard 'physically' away from the worker and ventilation that strategically 'adds' and 'removes' air in the work environment.

Personal Protective Equipment:

Eye/Face Protection: Chemical goggles. Full face shield may be required for supplementary but never for primary protection of eyes. Contact lenses may pose a special hazard; soft contact lenses may absorb and concentrate irritants. A written policy document, describing the wearing of lenses or restrictions on use, should be created for each workplace or task.

Hands/Feet Protection: Wear chemical protective gloves, e.g. PVC. Wear safety footwear or safety gumboots, e.g. rubber. The selection of suitable gloves does not only depend on the material, but also on further marks of quality which vary from manufacturer to manufacturer. Where the chemical is a preparation of several substances, the resistance of the glove material can not be calculated in advance and therefore has to be checked prior to the application. The exact break through times for substances has to be obtained from the manufacturer of the protective gloves and has to be observed when making a final choice. Personal hygiene is a key element of effective hand care. Use neoprene rubber gloves.

Other Protection: Overalls, PVC Apron, PVC protective suit may be required if severe exposure. Eye wash unit.

PHYSICAL & CHEMICAL PROPERTIES

Physical state:	Divided Solid
Colour:	White
Odour:	Slightly Pungent
Molecular Formula:	F2H5N
Solubility in water:	Soluble in water.
Specific Gravity:	1.50
Relative Vapour Density (air=1):	Not available.
Vapour Pressure (20 °C):	1 hPa
Flash Point (°C):	Not applicable.
Flammability Limits (%):	Not applicable.
Autoignition Temperature (°C):	Not applicable.
Solubility in water (g/L):	630 @20°C
Melting Point/Range (°C):	125
Boiling Point/Range (°C):	239.5
pH:	3.5 (5% solution)

STABILITY & REACTIVITY

Stability: Contact with alkaline material liberates heat. Unstable in the presence of incompatible materials. Product is considered stable. Hazardous polymerization will not occur.

TOXICOLOGICAL INFORMATION

Toxicological Effects

Inhaled: Inhalation of dusts, generated by the material, during the course of normal handling, may be harmful. Acute effects of fluoride inhalation include irritation of nose and throat, coughing and discomfort. A single acute over-exposure may even cause nose bleed. Corrosive acids can cause irritation of the respiratory tract, with coughing, choking and mucous membrane damage. There may be dizziness, headache, nausea and weakness. Persons with impaired respiratory function, airway diseases and conditions such as emphysema or chronic bronchitis, may incur further disability if excessive concentrations of particulate are inhaled. If prior damage to the circulatory or nervous system has occurred or if kidney damage has been sustained, proper screening should be conducted on individuals who may be exposed to further risk if handling and use of the material result in excessive exposures.

Ingestion: Toxic Effects may result from the accidental ingestion of the material; animal experiments indicate that ingestion of less than 40 grams may be fatal or may produce serious damage to the health of the individual. The material can produce chemical burns within the oral cavity and gastrointestinal tract following ingestion. Fluoride causes severe loss of calcium in the blood, with symptoms appearing several hours later including painful and rigid muscle contractions of the limbs. Cardiovascular collapse can occur and may cause death with increased heart rate and other heart rhythm irregularities. Ingestion of acidic corrosives may produce burns in and around the mouth, the throat and oesphagus. Immediate pain and difficulties in swallowing and speaking may also be evident. Acute ingestion of 3.75 grams (2.5 grams of fluoride ion) is estimated to be fatal for a human being. Ingestion may result in dehydration, thirst, nausea, vomiting, diarrhea, abdominal pain, gastrointestinal burns, headache and convulsions.

Skin Contact: The material can produce chemical burns following direct contact with the skin. Skin contact with the material may damage the health of the individual; systemic effects may result following absorption. Skin contact with acidic corrosives may result in pain and burns; these may be deep with distinct edges and may heal slowly with the formation of scar tissue. Fluorides are easily absorbed through the skin and cause death of soft tissue and erode bone. Healing is delayed and death of tissue may continue to spread beneath the skin. Open cuts, abraded or irritated skin should not be exposed to this material. Solution of

material in moisture on the skin, or perspiration, may markedly increase skin corrosion and accelerate tissue destruction. Entry into the blood stream, through, for example, cuts, abrasions or lesions, may produce systemic injury with harmful effects. Examine the skin prior to use of the material and ensure that any external damage is suitably protected.

Eye: The material can produce chemical burns to the eye following direct contact. Vapours or mists may be extremely irritating. If applied to the eyes, this material causes severe eye damage. Direct eye contact with acid corrosives may produce pain, tears, sensitivity to light and burns. Mild burns of the epithelia generally recover rapidly and completely.

Chronic: Substance accumulation, in the human body, may occur and cause some concern following repeated or long-term occupational exposure. Repeated or prolonged exposure to acids may result in the erosion of teeth, swelling and/or ulceration of mouth lining. Irritation of airways to lung, with cough, and inflammation of lung tissue often occurs. Extended exposure to inorganic fluorides causes fluorosis, which includes signs of joint pain and stiffness, tooth discolouration, nausea and vomiting, loss of appetite, diarrhea or constipation, weight loss, anaemia, weakness and general unwellness. There may also be frequent urination and thirst. Hydrogen fluoride easily penetrates the skin and causes destruction and corrosion of the bone and underlying tissue. Ingestion causes severe pains and burns in the mouth and throat, and blood calcium levels are dangerously reduced.

Ingredient	Toxicity	Irritation
Ammonium bifluoride	Inhalation (rat) LC50: 319 ppm/1hr*[2]	Eye (-): corrosive*
	Oral (rat) LD50: 130mg/kg[1]	Skin (-): corrosive*
Ammonium Fluoride	Not available	Not available
Hydrogen Fluoride	Inhalation (rat) LC50: 1276ppm/4hr[2]	Eye (human): 50mg SEVERE
	Inhalation (rat) LC50: 319 ppm/1hr[2]	
Ammonium fluorosilicate	Oral (mouse): LD50: 70mg/kg[2]	Not available
*Legend: 1. Value obtained from Europe ECHA Registered Substances – Acute Toxicity 2.*Value obtained from manufacturers SDS. Unless otherwise specified data extracted from RTECS – Register of Toxic Effect of chemical Substances*		

Ammonium Bifluoride – For acid mists, aerosols, vapours
Test results suggest that eukaryotic cells are susceptible to genetic damage when the pH falls to about 6.5. Cells from the respiratory tract have not been examined in this respect. Mucous secretion may protect the cells of the airway from direct exposure to inhaled acidic mists (which also protects the stomach lining from the hydrochloric acid secreted there). The material may produce moderate eye irritation leading to inflammation. Repeated or prolonged exposure to irritants may produce conjunctivitis. The material may produce respiratory tract irritation, and result in damage to the lung including reduced lung function. The material may cause skin irritation after prolonged or repeated exposure and may produce on contact, skin redness, swelling, the production of vesicles, scaling and thickening of the skin.

Hydrogen Fluoride – The material may produce severe irritation to the eye causing pronounced inflammation. Repeated or prolonged exposure to irritants may produce conjunctivitis.

Ammonium Bifluoride & Hydrogen Fluoride – Asthma-like symptoms may continue for months or even years after exposure to the material ends. This may be due to a non-allergic condition known as reactive airways dysfunction syndrome (RADS) which can occur after exposure to high levels of highly irritating compound. Main criteria for diagnosing RADS include the absence of previous airway disease in a non-atopic individual, with sudden onset of persistent asthma-like symptoms within minutes to hours of a documented exposure to the irritant. Other criteria for RADS include a reversible airflow pattern on lung

function tests, moderate to severe bronchial hyperactivity on methacholine challenge testing, and the lack of minimal lymphocytic inflammation, without eosinophilia.

ECOLOGICAL INFORMATION

Ingredient	Endpoint	Test Duration (HR)	Species	Value	Source
Ammonium bifluoride	LC50	96	Fish	0.068mg/L	2
	EC50	96	Crustacea	26-48mg/L	2
	NOEC	744	Fish	<0.048mg/L	2
Ammonium fluoride	LC50	96	Fish	51mg/L	2
	EC50	48	Crustacea	2.94mg/L	2
	EC50	96	Crustacea	26-48mg/L	2
	NOEC	672	Fish	0.17mg/L	2
Hydrogen fluoride	LC50	96	Fish	51mg/L	2
	EC50	48	Crustacea	=270mg/L	1
	EC50	96	Crustacea	26-48mg/L	2
	NOEC	504	Fish	4mg/L	2
Ammonium fluorosilicate	N/A	N/A	N/A	N/A	N/A

Legend: Extracted from 1. IUCLID Toxicity Data 2. Europe ECHA Registered Substances – Ecotoxicological Information – Aquatic Toxicity.

Ecotoxicity: The tolerance of water organisms towards pH margin and variation is diverse. Recommended pH values for test species listed in OECD guidelines are between 6.0 and almost 9. Acute testing with fish showed 96h-LC50 at about pH 3.5. For fluorides: small amounts of fluoride have beneficial effects however, excessive intake over long periods may cause dental and/or skeletal fluorosis. Fluorides are absorbed by humans following inhalation of workplace and ambient air that has been contaminated, ingestion of drinking water and foods and beverages prepared with the water. Amount these populations, outdoor labourers, people living in hot climates, and people with excessive thirst will generally have the highest daily intake of fluorides because they consume greater amounts of water. Prevent by any means possible, spillage from entering drains or water courses. Do NOT discharge into sewer or waterways.

Bio-accumulative potential: No data available.

Mobility in Soil: No data available.

DISPOSAL CONSIDERATIONS

Product/Packaging Disposal: Containers may still present a chemical hazard/danger when empty. Return to supplier for reuse/recycling if possible. Otherwise: If container can not be cleaned sufficiently well to ensure that residuals do not remain or if the container cannot be used to store the same product, then puncture containers, to prevent re-use, and bury at authorized landfill. Where possible retain label warnings and SDS and observe all notices pertaining to the product. Legislation addressing waste disposal requirements may differ by country/state and/or territory. Each user must refer to laws operating in their area. In some areas, certain wastes must be tracked. A hierarchy of controls seems to be common – the user should investigate – reduction, re-use, recycling, disposal (if all else fails). This material may be recycled if unused, or if it has not been contaminated so as to make it unsuitable for its intended use. Do NOT allow wash water from cleaning or process equipment to enter drains. It may be necessary to collect all wash water for treatment before disposal. In all cases disposal to sewer may be subject to local laws and regulations and these should be considered first. Where in doubt, contact the responsible authority. Recycle wherever possible. Consult manufacturer for recycling options or consult local or regional waste management authority for disposal if no suitable treatment or disposal facility can be identified. Treat and neutralize at an approved treatment plant. Treatment should involve: mixing or slurrying in water, neutralization with soda-lime or soda-ash followed by: burial in a land-fill specifically licenses to accept chemical and/or pharmaceutical wastes or incineration in a licensed apparatus (after admixture with

suitable combustible material). Decontaminate empty containers with 5% aqueous sodium hydroxide or soda ash, followed by water. For small quantities: cautiously dissolve in water, neutralize with sodium carbonate or if product does not dissolve completely add a small quantity of hydrochloric acid followed by sodium carbonate. Add excess calcium chloride to precipitate the fluoride and/or carbonate. Remove solids to site approved for hazardous waste.

TRANSPORT INFORMATION

UN Number: 1727
Proper Shipping Name: Ammonium Hydrogendifluoride, Solid
Class: 8 – Corrosive
Packing Group: II
Hazchem: 2X

REGULATORY INFORMATION

HSNO Classifications: 6.1C, 8.2C, 8.3A
EPA Approval: HSR002510

Restrictions: Ammonium Bifluoride has an Acute Toxicity – Category 3 classification (6.1C), therefore it is Restricted to Workplace only under the Hazardous Substances (Hazardous Property Controls) Notice 2017

OTHER INFORMATION

End of SDS.