Wet End Chemistry Essentials: Building the **Foundation of Paper Making**

Dr. Ashish Kumar Director







Paper making raw materials and fiber characteristics



Raw materials used in papermaking

- The raw material which is widely used in papermaking is pulp. Many types of fibers like cotton fiber and cellulose fiber are used to produce the paper pulp.
- It contains a good quantity of cellulose fibre which is a threadlike structure and acts as the building block of the final product.
- The pulp is mixed with different chemicals and papermaking agents to enhance the brightness, stability, water or liquid resistance ability, and removing the impurities out of it.

1. Pulp

The pulp is the basic and most important ingredient for papermaking. It is the major raw material that is used in the largest fraction with other materials. On the basis of their source medium, the pulp is again categorized as:

• Wood Pulp

There are two sources of wood pulp i.e. hardwood trees and softwood trees. More than 90% of the total manufactured paper is made from wood pulp today. Wood pulp is obtained by chemically or mechanically reducing wood fiber into a lignocellulosic fibrous material.

The various kinds of paper made from wood pulp are newspapers, magazines, toilet papers, etc. Softwood coniferous trees like pine and spruce are the richest source of wood pulp.

Non-Wood Pulp

like cotton, linen, or hemp fibers. Straw, bamboo and esparto grass are alternative materials accustomed to manufacture fibers.

Recycled Paper Pulp

Recycled paper pulp creates the one-third part of the total raw pulp. First of all, by using the deinking process the ink is separated from the recycled paper pulp and then it is mixed with the virgin pulp to produce different grades of recycled paper.

2. Sizing Elements

Starch and rosin sizing can be done both internally as well as externally. Rosin is used in internal sizing to provide the paper water-resistance and starch is used for surface sizing to control the absorption of printing ink and reduces the release of surface fibers.

3. Fillers Agents

To enhance the paper opacity, smoothness, and color mineral fillers are used. Fillers improves the brightness and whiteness of the paper and provides more pop to printing paper.

4. Pigments or Coloring Agents

Pigments are used to provide different colors to the paper in the paper industry. To colog paper, soluble pigments are used. Fluorescent pigments are extensively used in the paper coating process

Pulp parameters to be taken care of:-

- 1. Composition
- 2. Consistency
- 3. Pulp Draw
- 4. pH
- 5. Alkalinity
- 6. Colloidal charge
- 7. Zeta potential
- 8. Soda Carryover
- 9. Hexanueronic content

Stock and back water Parameters

- 1. pH: -ve logarithmic of hydrogen concentration
- 2. Consistency: Consistency is the percent of oven dry mass in the pulp
- 3. Freeness: Canadian Standard Freeness is the ability of water to drain through the pulp, measured as volume of water draining through side-orifice (units of mL) of CSF tester.

4. Alkalinity: The buffering capacity of a water body; a measure of the ability of the water body to neutralize acids and bases and thus maintain a fairly stable pH level"

P- Alkalinity M- Alkalinity

The concentration of ions in the water that neutralize the hydrogen ion is known as alkalinity. #he most well-known alkalinity components are bicarbonate, carbonate, and hydroxide, respectively



5. Hardness: The simple definition of water hardness is the amount of dissolved calcium and magnesium in the water. Hard water is high in dissolved minerals, largely calcium and magnesium.

6. First pass ash retention:

(Crucible + ash) weight – Crucible weight Ash content, % = ----- * 100 Handsheet weight

Handsheet ash, % First pass ash retention, % = ------ * 100 Buchner sheet ash, %

7. Ionic Behavior and Charge Demand of Pulp Slurry

The pulp slurry was filtered through 200 micrometer screen and 10 ml of the filtrate was taken as the sample. The charge was measured on Mutek PCD 03 pH Particle Charge Detector and the sample was titrated with cationic/ anionic polymer to neutralize the charge.

8. Zeta Potential of Pulp Slurry

About 500 ml pulp slurry (0.33% consistency) was taken and mixed thoroughly before measurement. The zeta potential of the pulp slurry was measured and the value is denoted in mV.



Fibre unit structure





Fig. 1. Fibre unit structure: (a) schematic of cell wall layers (middle lamella (ML), primary wall (P), secondry wal (S1, S2, S3) and lumen (W); (b) fibrillar structure of cell wall; (c) scanning microscopic image of cell wall layers; and (d) scanning microscopic image of microfibrils (Chinga-Carrasco, 2011; Fardim, Liebert & Heinze, 2013; Fellers & Norman, 1998; Page, 1989a,b; Sixta, 2008).

The cell wall structure (Fig. 1) of different species is generally composed of cellulose, hemicelluloses and lignin. Cellulose is a polysaccharide consisting of glucose units.

Cellulose has crystalline structure while hemicellulose has amorphous structure. Hemicellulose surrounds cellulose microfibrils. Hemicellulose has a lower strength than cellulose and can be easily hydrolyzed.

The third component of the cell wall is lignin. Lignin acts as glue and binds the different layers of cell wall. Lignin is a hydrophobic substance and can be removed by chemical pulping and bleaching.

All of these components are present in the different layers of cell wall. The cell wall can be divided into different layers: middle lamella (ML), primary cell wall, secondary cell wall and lumen.

Types of pulping

- To produce the pulp from the raw materials, different pulping processes can be performed on the chips or small parts which have been produced by the chipping of timber or other parts of plant.
- Depending on the pulping processes the wood pulps are categorized as mechanical pulp, chemical pulp (e.g., kraft, sulfite pulps) and chemithermomechanical pulp (CTMP). Mechanical pulps are produced from raw material by the application of mechanical energy. Chemical pulps are almost pure celluloses which are produced by heat and chemical treatment.
- Thermomechanical pulps (TMP) are one of the popular types of mechanical pulps which are produced by processing the wood chips using the high temperature steam and mechanical refining. During the treatment of raw material with chemicals, a large amount of lignin is extracted from the material

Pulp Refining

One of the processes that is conducted in the stock preparation is so-called "pulp refining" or "beating". Pulp refining or beating could be described as a mechanical treatment of the pulp by using the special equipment in the refining process, the fibers are under compression and shear forces which are causing several changes in specifications of fibers.



Changes happen to the electro-kinetic properties of fiber during pulp refining

Wood fibers develop a negative surface charge when suspended in water. The level of anionic charge on the pulp supplied from the pulp mill is typically –20 to –25 mV depending on the level of carboxyl acid groups present in the pulp, which depends upon the source of fibers, and some chemical treatments applied in the pulping process. For example, hardwood pulps have a higher surface charge and total charge density than softwood pulps.

Two mechanisms: (i) presence of ionizable groups in the fiber cellulose such as carboxylic acids, sulfonic acidic, and functional groups in lignin, (ii) adsorption of suitable ions, have been introduced by researchers as a responsible for surface charge development.

Refining increases the surface charge while it has no considerable influence on the total charge. It is widely known that charge groups affect the fiber swelling, fiber flexibility and conformability, wetend chemistry, retention of cationic papermaking additives, flocculation and mechanical properties of the paper such as tensile index thus the measurement of the charges is a subject of interest. To obtain the charges, some methods based on titration are recommended, such as polyelectrolyte titration, conductometric titration and potentiometric titration.







Wet end chemistry

Wet end chemistry is focused on two objectives

- Achievement of paper properties
- Enhancement of paper machine runnability The first objective is aimed at meeting product specifications set by customers.

The second category is most important to paper machine productivity.

Paper properties

- Structural properties (Basis weight, caliper, formation, directionality, two sidedness, porosity, roughness)
- Mechanical properties (tear, tensile, burst, stiffness, folding endurance, internal bonding strength, surface strength)
- Appearance properties (color, brightness, opacity, gloss)
- Barrier and resistance properties (sizing)
- Permanence properties (durability, color reversion)





Introduction

When studying a broad subject like wet end chemistry, it is helpful to identify the major themes that tie the material together. The following four examples are particularly relevant

• The importance of chemical equilibria.

Many wet-end chemistry phenomena are based on chemical equilibria and so the papermaker needs to be well grounded in these fundamental concepts.

The importance of particle specific surface area

Surface interaction such as adsorption, aggregation, and ion exchange are extremely important in wet end chemistry. All of these phenomena are affected by the specific surface area of participating fibers, fines and fillers.

The role of surface as well as dissolved charge

All papermaking furnish components have associated electrostatic charges that play important roles in adsorption and aggregation processes.

The adverse effect of interfering substances

The interfering substances interfere with most functional additives and some processing aids. A papermaker must be aware of their existence and be knowledgeable about their properties and understand how to counteract them in a given situation.



Surface and colloidal science concepts



Interface and colloid science is that branch of chemistry, which deals with the study and application of colloids, heterogeneous systemic mechanical mixtures of particles between 1nm and 1000nm dispersed in a continuous medium.

Colloidal state

When the surface chemical properties of a dispersed system are important to the overall chemical ehavior of the system, the study of the system involves a branch of physical chemistry known as olloidal chemistry. Thus paper making chemistry is really colloid chemistry because of the large pecific areas involved and because most papermaking chemistry occur at particle surface.

Classification systems in colloid chemistry

Hydrophobic

- All pigments dispersed in water
- Fines dispersed in water
- Rosin size in water
- Dispersed rosin size emulsion

Hydrophilic

- Starch dissolved in water
- Gums dissolved in water
- Hemicelluloses dissolved in water
- Surfactants dispersants, wetting agents dissolved in water
- Retention drainage and formation aids dissolved in water



Surface charge on hydrophobic particles

- An electrostatic charge on hydrophobic particles develops at the solid water interface when solids are dispersed in water. In paper making systems, this charge may arise from dissociated surface carboxyls and sulfonic acid groups and the adsorption of substances such as hemicelluloses, dissolved lignin, retention aids and cationic starches onto surfaces.
- lons of opposite charge to that of the particle surface (counterions) are held closely adjacent to the surface by electrostatic and Vander Waals forces. The potential energy drops off in this region rapidly. A hydrodynamic slip plane exists between the tightly bound counterions and solvent molecules adjacent to the surface (Stern Layer) and rest of the solution
- The less ordered, diffuse portion of the system is called the Gouy-Chapman Region. The potential falls off at a slower rate in this region than in the Stern layer.
- The potential at the interface plane between the stern layer and Gouvy

Electrical double layer existing at the surface of hydrophobic particles suspended in water



- 1. IHP Inner Helmholtz Layer 2. Outer Helmholtz Layer
- 3. Diffuse layer 4. Solvated ions 5. Peculiar adsorptive ions
- 6. Solvent molecule.





Aggregation and stabilization of hydrophobic dispersions



Aggregation and stabilization of hydrophobic dispersions

a. Coagulation by charge neutralization

- A layer of strongly adsorbed counter ions and a diffuse region of counter and co-ions make up the electrical double layer of particles suspended in water.
- The thickness of the double layer decreases when electrolytes are added to the suspension due to an increase in the availability and number of counter ions.
- Increased counter ions concentration reduces the zeta potential.
- Particles can then approach more easily and aggregation becomes more likely. Aggregation by this mechanism is referred to as charge neutralization because the addition of excess counter ions moves the net potential towards a state of zero charge.
- Charge neutralization is a coagulation phenomenon.



Aggregation and stabilization of hydrophobic dispersions contd.

b) Patch replica

- When low molecular weight cationic poly electrolytes with high charge density are mixed with anionic particles, the polymer molecules are believed to adsorb completely on to the particle surfaces and form a patch of positive charge. This patch effectively reverses the anionic charge at that site on the particle surface while the rest of the particle remains anionic.
- After the polyelectrolyte is adsorbed, collision of the positively charged patch with an uncovered negative area on another particle leads to coagulation





Aggregation and stabilization of hydrophobic dispersions contd.

C) Bridging flocculation behavior

- The flocculation of colloidal material by polyelectrolyte of high molecular weight is presumed to take place by a bridging mechanism
- The polymer adsorbs on to the surface with a series of loops and tails.
- Flocculation then occurs by adsorption of the extended loops and tails on to the negative surface of the second particle





Factors that affect Polyelectrolyte adsorption

- Polymer characteristics:- Charge density, Molecular weight, Chain length
- Fiber characteristics:- Available adsorption sites, surface charge, surface area, fines content
- Chemical environment:- pH, conductivity, interfering substances, anionic polymers.
- Physical environment:- Shear and turbulence, furnish consistency, order of addition



Interfering substances

Fresh water

- Calcium and magnesium hardness
- Organic matter
- Residual chlorine
- Suspended solids

Pulping residuals

- Sodium salts
- Rosin soaps
- Fatty acid soaps
- Lignin compounds

Bleaching residuals

- Sodium salts
- Calcium salts from calcium hypochlorite
- Alkali soluble cellulose and hemicelluloses

Broke

Starch, adhesives, inks and coating components





Effect of Interfering substances

Conductivity:- It is the measurement of dissolved ions High levels = High conductivity High conductivity = Bad news

- Reduces charge on particles
- Reduces affinity for charged polymers
- Reduces efficiency of polymer

Charge:- Most colloidal interfering substances are anionic High amount (Anionic trash) = Bad news





Charge/Zeta potential measurement and their importance







Why are papermakers so interested in charge measurement?

The charge on collo stability of their dispersi making materials play key roles in many wet end chemistry phenomena and the measurement and control of these charges is a key element in wet end chemistry process control

is a key element in wet end chemistry process control.



Sources and nature of electrostatic charge on paper making materials

- Fibers
- Fiber fines
- Fillers
- Retention aids
- Dry strength resins
- Wet strength resins
- Wood lignin & hemicelluloses
- Dispersants
- Alum

Here surface as well as dissolved charge both play important and different roles in wet end chemistry process control.

Measurement of Surface charge of suspended paper making particles (Electro kinetic measurement)

Methods to measure Surface charge of papermaking particle

- Micro electrophoresis
- Streaming potential
- AC streaming current

Streaming potential

In streaming potential measurement, liquid is forced under a pressure gradient through a plug formed from fibers, fines and other furnish components. Electrodes are placed on either side of the plug to measure the streaming potential established across the plug by the flowing liquid.



Figure 1: Schematic showing the distribution of ions around a charged particle.



Dissolved/ Soluble charge Measurement

The term Anionic trash and cationic demand appeared in 1970's when environmental legislation required papermakers to close white water systems and reuse it. This practice leads to increased concentration of dissolved and suspended solids in mill water. Many of the dissolved and suspended substances are colloidal and carried anionic charges, they reacted with cationic additives and reduced their effectiveness

Colloid titration

Colloid titration usually involves titrating a sample with a standard cationic or anionic polymer that will react with its oppositely charged counterpart in the sample to form a one to one charge complex. An end point detection method is employed that indicates the point at which the first bit of excess titrant is added. The amount of titrant charge added up to that point is equal to the amount of oppositely charged, dissolved charge in the sample



One to one charge complex formation



Polymer complex



Application of Charge measurement of paper making

Recent years have seen greatly increased application of charge measurement by paper makers and chemicals suppliers.

a)Application of offline charge measurements

Chemical suppliers and papermakers are using colloid titration and micro electrophoresis data to guide them in setting product addition rates and for trouble shooting wet end chemistry process and product problems (retention, sizing, coloring drainage, opacity brightness). One particularly wide spread use of colloid titration is in the determination of interfering substances in process stream

b) Application of online charge measurement

One application of online monitoring involves the inverse correlation between variability in head box zeta potential and paper machine run ability. The greater the variability, the poorer the run ability.

Online measurement on process feed streams can also be used to reduce the electro kinetic variability of the head box furnish. The parameters that are essentially be monitored

- ZP before and after chemical addition point to determine their interaction with fibers and fines
- Cationic demand and ZP variability of incoming broke and pulp streams- both before and after treatment.





The importance of maintaining a constant head box ZP on the slightly negative side is strongly emphasized.

A slight negative charge is preferred because this situation indicates that one has not overdosed cationic additives at points leading up to the head box.

If one tries to control to a neutral ZP then the possibility of overshooting on the cationic side exists.





Wet-end additives and their effect on process and paper properties



Intro



Because of the special effect of water on paper strength, it is common to distinguish between the dry strength and wet strength properties of paper.

Paper strength is affected by many furnish and process variables.

On the furnish side

- longer the softwood fibers produce stronger papers than shorter hardwood fibers.
- Fillers reduces the strength.
- Alkaline pH conditions produce stronger paper than acid pH.

On the process side

 Increased wet pressing and refining both increase paper strength.

Widespread Dry Strength Additives



Many water soluble, hydrogen bonding polymers will act as dry strength additives. Hemicelluloses is the naturally occurring dry strength additive present in the wood fiber. It is intricate to develop bonding characteristics without hemicelluloses. e.g. it is hard to achieve inter fiber bonding in paper produced from cotton fiber- which has no hemicelluloses

The three most common commercial types dry strength additives in use today

- Starch derivatives (95%)
- Gums (Mannogalactans) (2%)
- Synthetic dry strength agents (2%)

Other substances such as unmodified and anionic starched, soluble cellulose derivatives, wet strength resins, polyvinyl alcohol and latex account for the remaining one percent of DSA.



Utilization of Cationic starch as DSA

- Different type of starches have been used to increase paper strength in paper machines for many years. To start with, wet end addition of native starches was used for strength improvements, but since this type of starch shows a low affinity for cellulosic fibres and also resulted in a high BOD load in the effluent water. Introduction of cationic starches lead to a dramatic improvement in dry strength, resulting in cationic starch becoming the most utilised product for strength improvements in the paper industry.
- For maximum strength improvement, cationic starches should be added to the thick stock where they must react for several minutes with the furnish components. The maximum dosage of cationic starch is limited to about 1.5%
- Overuse of high DS cationic starch can, in some cases, adverse effect the charge balance at the wet end causing difficulties with the substantivity of other cationic charged species or functional chemicals

Utilization of Cationic starch as DSA contd...

- Starch is composed of two different macromolecules, Amylose and Amylopectin.
- Amylose is a linear or sparsely branched carbohydrate with a molecular weight of 105-106.
- Amylopectin is a highly multiple-branched polymer with a high molecular weight: 107-109.

It is necessary to attach cationic substituent's to the native starch structure in order to achieve the high retention level required in papermaking. Starches are cationized with either tertiary or quaternary amine groups. The common reagents for imparting cationic character to starch are as follows

- 2-chloroethyldiethyl amine
- 3 chloro-2 hydroxypropyltrimethylammonium chloride
- 2,3-Epoxypropyltrimethylammonium chloride



Structure of starch components



Amphoteric starches as DSA

- Jps.
- Amphoteric starches contain both cationic and anionic groups.
- In general, cationic groups may be amino, immonium, ammonium, sulphonium or phosphonium, but at the present tertiary amino groups or quaternary ammonium groups are the most important industrial positive groups
- Anionic groups are usually carboxyl groups, phosphate groups or sulfonate groups
- These are useful when a furnish would become over cationized if a cationic starch were utilized
- They are capable of tying up cations such as ca⁺² Mg⁺²



Two-step mode for preparation of amphoteric starches



X+ : Cationizing reagentY- : Anionizing reagent





Amphoteric Starch

- Amine groups (blue), % N 0.2 to 0.33
- Phosphate groups (red), usually at lower level than the amine groups.







Mechanism of strength development



Mechanism of strength development

- Starch enhances interfiber bonding
- Its free glucose hydroxyls participate in hydrogen bonding with fiber surface cellulose molecules and supplement the number of H-bonds (Chemical hydration of fiber system)
- The decrease in tear strength that normally accompanies refining can be alleviated by the use of dry strength additives
- A second mechanism involves the improvement of sheet formation by providing more uniformly distributed fiber-fiber bonds
- A third less important mechanism involves the improved web consolidation that occurs when dry strength agents enhance fines retention and sheet dewatering

Effect of starch charge density and dosage levels on adsorption

- Natural neutral starch retains to a very low degree on fibers since there is very little attraction
- Adding a cationic charge to the starch molecule creates attractive forces between starch
 and anionic fiber surface thus increasing adsorption rate
- As the DS of starch increases, a point is reached where adsorption reaches a maximum & then declines (This point is a combined function of charge density & dosage level)
- When the charge density becomes so high then the fiber gets overcharged then the attraction between the starch molecules and fiber surface declines.
- Higher the dosage rate sooner this point is reached. Paper makers then must pay close attention to both dose level and starch charge density when using this material in order to achieve high efficiencies
- Starch adsorption capacity of fibers can be increased by increasing the anionic character of the surface



Polyacrylamide as Dry Strength resins



- These are the water soluble polymers which contain primary amide groups that forms H- bond with cellulose molecules and improve interfiber bonding.
- The Polyacrylamide structure shown below is a nonionic material having very little attraction to papermaking fibers and can't be retained as such so it is necessary to incorporate some kind of charged group in the polymer structure





Anionic & cationic Polyacrylamide

Anionic Poly.

- The amide (CONH₂) group is replaced by COOH.
- The carboxylic group is ionizable and introduced in polymer chain (or by alkaline hydrolysis of amide group).
- The extent of ionization is pH dependent so in acidic condition only a fraction of it is ionized, while if pH is increased up to 8-8.5 anionic Polyacrylamide are completely charged with anionicity.

Cationic poly.

- Cationic promoters (Alum & PAC) are used in conjunction with anionic poly or the cationic group is directly incorporated in the Polyacrylamide backbone.
- Cationic Polyacrylamide are produced by either copolymerization with cationic monomers or by modifying some of the amide group to the cationic groups.
- Unlike anionic polymer cationic Polyacrylamide are completely ionized over entire pH range.







Wet strength additives



Wet strength additives

Paper lost most of its strength when it is in contact with water and fiber fiber bonds are replaced with fiber- water bonds. Wet strength additives like DSA are polymeric materials that must be adsorbed by furnish components in order to be effective.

Most commonly used wet strength resins

- Urea Formaldehyde
- Melamine Formaldehyde
- Polyamide Epichlorohydrin
- Polyamine- Epichlorohydrin



Wet strength mechanism

In order for paper to retain its strength when wet, it is necessary to take one or more of the following actions

- Strengthen the existing bonds
- Protect existing bonds
- Form bonds that are insensitive to water
- Produce a network of material that intermingles with fibers

The above phenomenon is achieved by the following mechanism Create a cross linked network within and around fibers that inhibits swelling and water sorption and protects existing interfiber H- bonds (Homo cross linking mechanism)

Create new water resistant interfiber bonds such as covalent, acetal, hydrogen bonds that cross link fibers (**Co-cross linking mechanism**)



Variables important to the retention of wet strength resins

- Fiber anionic sites
- Pulp consistency
- Contact time
- Resin dilution
- Pulp refining





Latest developments in wet-end applications



Latest developments in wet-end applications

- Nanotechnology has been used to improve retention and drainage systems for wetend chemistry (e.g. Addition of cationic starch and colloidal silica to slurries of fibres.)
 The benefits of silicate nanoparticle retention and drainage systems
- Improved formation; retention; drainage; dry strength; Better reactivity. Increased production; Reduced steam consumption; Products with higher brightness (Ref:-Nanotechnology in wet end chemistry Written by Martin E Hubbe)
- Replacement of clay and titanium dioxide fillers by calcium carbonate with a parallel increase in loading levels
- Conversion of fine papermaking from acid to alkaline conditions
- Increased paper recycling
- Reduced fresh-water use
- New online sensors are being developed and papermakers are experimenting with new process control strategies and incorporating wet end chemistry process control with other paper machine control schemes

contd..

- Efforts to enhance the performance of wet end additives e.g. moving starch charges up and down and fractionation of molecules to get wider or narrower distributions of structures, slight changes to filler particle shape and distribution, and some effort to make fillers effective over a broader ph range
- The improved understanding we now have of charge levels, we now know how much negative charge there is in a pulp or water stream, in other words how much cationic chemical a given amount of water can absorb
- Single- and dual-component retention aid systems
- Deposit control systems for both acid and alkaline papermaking



- Optimization of both ASA and AKD sizing systems
- Interactions of wet-end chemicals with virgin and recycled fibers and fillers (clay, calcium carbonates, TiO2, and others).
- Manufacture of fine and specialty papers using recycled paper products and recycled pulps in both acid and alkaline papermaking systems
- Stickies control" system for recycled paper grades saving considerable costs in down time.
- Europe and the far east may be a little bit ahead of the united states in new developments for wet end chemistry, but there is still nothing to write home about

(Ref:-<u>http://www.intota.com/expert</u>-consultant.asp? bioID=603475&per ID=107636)



References



- A Review of Amphoteric Starches in Preparation and Applications ZHANG Min1,2, ZHANG Shu-fen1,*, JU Ben-zhi1, YANG Jin-zong1 (1State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, 116012, China. 2Dalian Fisheries University, Dalian, 116023, China)
- Principles of wet end chemistry by: William E. Scott
- Nanotechnology in wet end chemistry Written by Martin E Hubbe
- <u>http://www.intota.com/expert</u>-consultant.asp?bioID=603475&per ID=107636)









